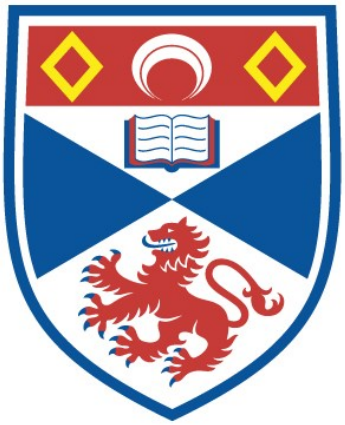
CYCLOPENTADIENYLIDES

John Stuart Sneezum

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1959

CYCLOPENTADIENYLIDES

being a thesis presented by

JOHN STUART SNEEZUM B.Sc.

to the University of St. Andrews

in application for the degree of

Doctor of Philosophy.

ms 2140

DECLARATION.

I hereby declare this Thesis to be based on the results of experiments carried out by me, and furthermore that the Thesis is of my own composition and has not previously been presented for a Higher Degree.

The investigation was conducted in the Chemical Research Laboratories of the United College in the University of St. Andrews, under the direction of D.M.G. Lloyd, B.Sc., A.R.I.C.

CERTIFICATE.

I hereby certify that Mr. John Stuart Sneezum, B.Sc., has spent ten terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Ph.D.

Director of Research.

UNIVERSITY CAREER.

I entered the University of St. Andrews as an undergraduate in October 1950, gained a pass B.Sc. in Chemistry and Mathematics in 1953 and graduated B.Sc. with Second Class Honours in Chemistry in July 1954.

The researches described in this thesis were carried out in the period between October 1954 and September 1957.

I was awarded a University Post-Graduate Scholarship and a D.S.I.R. Maintenance grant, which I held throughout this period.

PUBLICATIONS.

The preparation of a cyclopentadienylide.

Lloyd and Sneezum. Chem. and Ind. 1955, 1221.

The preparation of some Pyridinium cyclopentadienylides.

Lloyd and Sneezum. Tetrahedron, 1958. Vol. 3, pp. 334 - 338.

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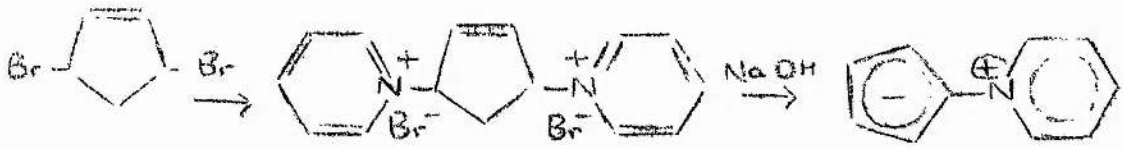
He is also grateful to the other members of the St. Andrews Chemistry Department for their cheerful assistance from time to time.

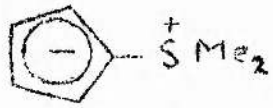
SUMMARY.

Cyclopentadienylides (e.g. (III)) were prepared from dibromocyclopentene (I) by the action of cyclic organic bases followed by treatment with caustic alkali. The intermediate was shown to be the dibromide of the diquaternary salt (e.g. (II)), and the reaction scheme may be represented, in the case of pyridine, by the equations:



I II III

These ylides are brown-red crystalline solids, which impart strong colours to their solutions. The colour varied with polarity of the solvent, e.g. from orange-red in alcohol to a slightly purplish-red in benzene. The reactions of various organic bases with dibromocyclopentene were investigated but satisfactory products were obtained only from pyridine and substituted pyridines. However, red materials of uncertain composition were obtained from aniline and ammonia. Also a compound from dimethyl sulphide was obtained, probably having the structure (IV) although satisfactory analysis results were not obtained in this case.



IV

The structure of the ylide from pyridine was established by catalytic hydrogenation to N-cyclopentylpiperidine and comparison of derivatives obtained therefrom with those from an authentic sample.

Tetraphenylcyclopentadienylides were prepared from 1-bromo-2:3:4:5-tetraphenylcyclopentadiene by allowing this bromo compound to stand with the bases at room temperature, and removing the elements of hydrogen bromide with sodium hydroxide. Ylides formed in this way were blue to blueish-purple crystalline solids, showing a corresponding range of colour in organic solvents.

The unphenylated ylides decomposed fairly rapidly on exposure to the air in the solid state, but more slowly in solution. The phenylated derivatives were quite stable as solids, but the colour of their solution faded quickly. Stability was enhanced in each case by storing the samples under nitrogen or in vacuo.

Derivatives were generally difficult to isolate, but compounds were obtained with picric acid (from phenylated ylides) and benzene diazonium chloride (from unphenylated ylides, including that from dimethyl sulphide).

A preliminary investigation was also made into the possibility of preparing many membered carbon rings by pinacone reduction of α-ω-diketones. α-ω-heptadecane dicarboxyclic acid was prepared as an intermediate.

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I. INTRODUCTORY.

The original intention was to investigate two topics concurrently, namely:-

(a) the preparation of many membered carbon rings by the method of pinacone reduction,

and (b) the formation and properties of cyclopentadienylides.

After some preliminary work had been done on both topics, the results obtained from the topic (b) showed promise of considerable interest and so attention was concentrated on this, and the bulk of this thesis is devoted to it. Discussion of the First topic is included as an appendix.

During the last few years there has been much work on and interest in the subject of non-benzene aromatic compounds with other than six-membered rings which show to a greater or lesser extent the aromatic properties associated with benzene. A large volume of information has been assembled about such compounds as the azulenes, tropolones and fulvenes; another important step was the somewhat fortuitous discovery of ferrocene.

Relatively little study had been made until recently of the possible aromatic compounds having a negatively charged five-membered ring, with the exception of the ferrocenes. Shortly before the present work began,

Doering and Depuy(46) published a synthesis of diazo-cyclopentadiene(I)

I

The object of the present researches was to explore this topic, particularly with regard to the possibility of obtaining compounds with a dipolar structure the so-called cyclopentadienylides, wherein the negative charge on the five-membered ring is balanced by a positive charge on some exocyclic group which is linked to the ring by means of a polar bond.

Such systems would be expected to show some degree of aromaticity. In the next section the concept of aromaticity, and especially its application to non-benzenoid systems is discussed.

II. HISTORICAL SURVEY.

1. The development of the Idea of Aromaticity.

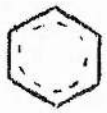
The reduced unsaturation of many compounds having particular arrangements of alternate double and single bonds has long posed a problem to theoretical chemists. This reduced unsaturation is very marked in benzene, which reacts more commonly by substitution rather than addition. Kekule(1) recognised as far back as 1865 that in the series of "aromatic" compounds, which had a much higher percentage composition of carbon than the fatty or aliphatic compounds, degradation always left a unit of at least six carbon atoms. This suggested a nucleus of six carbon atoms linked in some different and stabilised manner. Kekule's postulation of these six carbon atoms being joined in a closed chain laid the foundation of practically all aromatic chemistry.

However, the formulation (Ia, Ib) of benzene as a closed chain compound with each carbon atom holding one hydrogen, and having one double and one single bond attachment to its neighbours is not satisfactory as a substance with such a structure might be expected to show extreme unsaturation.

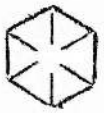
Ia

Ib

Various suggestions have been advanced to explain the actual state of affairs in benzene, but all of them have been shown to have shortcomings. Kekule imagined oscillation or tautomerism between the two forms, and this accounted for the absence of isomeric orthodisubstituted benzene derivatives. His representation comes close to that given by the Theory of Resonance. Modern views were perhaps more closely foreshadowed by Thiele's partial valency formula, Ic. The centric formula, Id, also helped to illustrate the equivalence of the six carbon atoms.



Ic



Id

X-ray analysis shows that the six carbon atoms in benzene are in a plane, equidistantly spaced at 1.39 A apart, between the normal 1.54 A single bond and 1.34 A double bond distances.

One of the theories which have attempted to combine these features is that of Resonance. It provides that the nuclei of the atoms concerned shall remain fixed and the electrons "move" between set formal structures (or canonical forms) which are all of the same magnitude energetically, and at the same time give rise to a molecule energetically stabilised with respect to any of them. This extra energy is described as the resonance energy.

In the case of benzene this difference, calculated from the heats of hydrogenation and the strength of three C-C double bonds, is approximately 39 Kg.cals/mole.

Open chain conjugated dienes and polyenes also show a modification of double bond character as compared with ethylene and the resonance energy of such a conjugated diene is estimated at 3 Kg.cals/mole. The effect of this conjugation is illustrated by the 1:4 addition of bromine to 1:3 butadiene. Benzene represents an extreme case of a conjugated polyene, as the alternate arrangement of the double bonds in the ring allows for continual or progressive interaction of the double bonds round the ring.

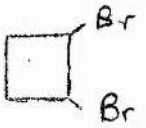
The distinction between the terms "conjugated" and "alternate" as applied to double and single bond systems should be noted. Conjugation involves interaction, or resonance, between the π-electrons, but in some cases steric factors prevent resonance interaction in a system of alternate double and single bonds.

If the only prerequisite for aromaticity were such a closed cyclic arrangement of double and single bonds, cyclobutadiene and cyclooctatetraene would be expected to exhibit aromatic properties.

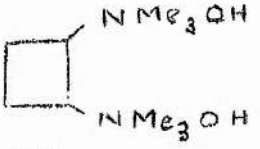
Cyclobutadiene (II) has as yet resisted all attempts at its preparation. This does not necessarily mean that it is too unstable to exist, but one might expect that a molecule stabilised by aromatic resonance would be formed

if a suitable reaction were applied to an intermediate having the correct skeleton. Nevertheless treatment of 1:2 dibromocyclobutane (III) with potassium hydroxide (2), and thermal decomposition (3) of the bisquaternary ammonium hydroxide (IV) yielded no cyclobutadiene.

II

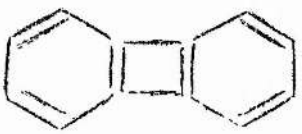


III

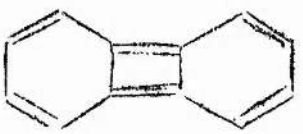


IV

The dibenzo derivative diphenylene has been prepared by Lothrop (4) by distillation of 2:2'-dibromo- or 2:2'-diiodo-diphenyl with cuprous oxide, and by Wittig and Herwig (5) by heating diphenylene mercury with silver powder. Diphenylene is a stable yellow solid m.p. 110°C, and possible canonical forms for it are Va-e.



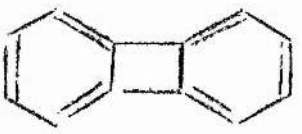
Va



Vb

Vc

Vd

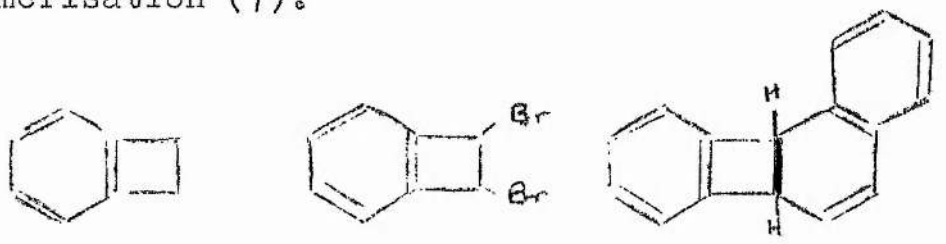


Ve

The first two show a cyclobutadiene system, but only the second one is a real cyclobutadiene, the others being merely benzene rings linked in the ortho positions. The complexity of the ultraviolet spectrum indicates that there

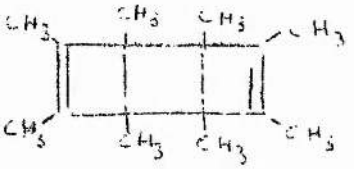
is something more than two linked benzene rings present, so that the four-membered ring may be to some extent cyclobutadenoid.

The monobenzo derivative of cyclobutene (VI) (6), and its dibromo derivative (VII) (6,7) are known. Treatment of the dibromo compound with zinc in ethanol gave a dihydro derivative of 1:2-benzodiphenylene (VIII), possibly by intermediate formation of benzocyclobutadiene followed by dimerisation (7).



VI VII VIII

More recently Criegree and Louis (8) have reported the preparation of the dimer of tetramethylcyclobutadiene, which they formulated as IX.



IX

This was formed as a high melting crystalline solid in an attempt to make tetramethylcyclobutadiene from the dichloro derivative of tetramethylcyclobutene, by shaking it with lithium amalgam in ether.

Although the central ring in diphenylene is highly strained, it does not readily react by addition to give diphenyl derivatives but can be hydrogenated in the presence of Raney nickel to give diphenyl.

In contrast to cyclobutadiene, cyclooctatetraene has been known since 1911 when it was prepared by Willstätter (9), by a method consisting essentially of successive Hofmann exhaustive methylations on pseudopelletierine. Although suggestions were made that Willstätter's product was not cyclooctatetraene but styrene, the work was confirmed in 1947 by Cope and Overberger (10), and during the Second World War, Reppe (11) prepared it on a large scale by catalytic polymerisation of acetylene. It is an unstable yellow liquid, which undergoes addition reactions; in some cases transannular rearrangement leads to bicyclic products. It cannot therefore be considered to be aromatic, and it has a very low resonance energy.

This lack of aromaticity in four- and eight-membered rings indicates that factors other than cyclic conjugation must be of importance. Many organic systems other than benzene show aromatic properties to a greater or lesser degree, common examples being the heterocycles furan, pyrrole and pyridine. Bamberger (12) associated this sort of behaviour with six "residual" valencies, and

later Armit and Robinson (13), in their study of anhydronium bases, recognised the importance of the aromatic sextet of π-electrons, although they did not then refer to them by this name.

E. Hückel (14) using resonance and molecular orbital theory, put the matter on a more general basis by postulating that aromaticity would be possible in a cyclic polyolefin containing $(4n+2)$ π-electrons where n=0,1,2,----- The significance of the sextet of π-electrons in benzene was justified in an approximate evaluation of the resonance energy of benzene. The treatment is described in Chapter II.2.

In the same way that olefinic bonds may be represented as having an electron-cloud above and below the bonds, so in benzene the π-electrons are visualised as having high density in space above and below the plane and round the periphery of the ring, and none in the plane of the ring.

The trigonally hybridised bonds in an olefine lie in a plane at 120° to each other so that in benzene there is no angular strain. In the five and seven membered rings the strain is small, but in some of the higher rings it can have a marked effect. Two conflicting influences thus come to bear - the tendency for a ring to become buckled to lessen angular strain and the tendency to form a planar

ring to allow the possibility of resonance, and consequent stabilisation. Another factor mitigating against the formation of a planar ring comes with the steric interference of the 'central' hydrogen atoms in larger rings, which can ease their strain by forming, for example, crown or star shaped molecules. No aromatic ring with more than seven carbon atoms has yet been prepared, and it has been predicted by Hislow (15), from scale drawings, that the smallest ring likely to be conjugated is $C_{30}H_{30}$, for which a resonance energy of 140 Kg.cals/mole has been calculated.

The criteria for aromaticity thus emerge as:-

(a) The possession of the correct number of π-electrons (i.e. six in the simple case).

(b) The molecule must be planar.

(c) The bond angles must not be very highly strained.

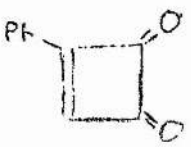
Cyclobutadiene and cyclooctatetraene do not comply with the first requirement, which could explain the absence of aromatic character.

Also, in cyclooctatetraene the molecule may assume the tub-shaped form, X, in order to lessen angular strain. This allows each of the four olefine groups to take up the arrangement as in ethylene, with all its bonds in a plane, and at 120° to each other. This gives an alternate

double and single bond system in which resonance interaction of the π-electrons is sterically inhibited.

X

Roberts and Smutny (84) have shown that excessive ring strain is not the reason for the non-existence of cyclobutadiene, by preparing phenylcyclobutadienequinone, XI, which would be expected to have a ring strain comparable with that in cyclobutadiene. Longuet-Higgins (16) has pointed out that in cyclobutadiene there would be only two electrons in the doubly degenerate orbital next above the ground state, giving an open shell structure.



XI

To illustrate the variety of possible aromatic ring systems, Baker (32) has pointed out that the -CH= groupings in benzene may be replaced by other specified groups with retention of the aromatic sextet. These groups may be classified as follows:-

To replace one -CH= grouping:-

1 =N- pyridine 1 $=\overset{+}{O}-$ (pyrylium salts)

1 $=CH-\overset{+}{C}H-$ (cycloheptatrienylium salts, tropone)

To replace 2 -CH= groupings:-

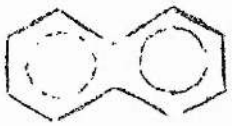
1 -$\overline{C}$- (cyclopentadienyl)

1 -NH- (pyrrole)

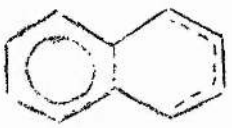
1 -S- (thiophen)

In particular it will be seen that the five- and seven- membered carbocycles fulfil the conditions, when associated respectively with negative and positive charges.

The application of the sextet rule to polycyclic systems is less straightforward, as the individual rings can only have a share in a sextet. Thus in the case of naphthalene we may express the electronic arrangement as XIIa, which is rather unrealistic in ignoring the middle C-C bond, or as XIIb, which goes some way to interpreting its chemical reactivity, and its hydrogenation to form a tetrahydro compound.



XII a



XII b

Some of the first known non-benzenoid aromatic compounds were the azulenes, but only more recently has the full background of their behaviour been realised as

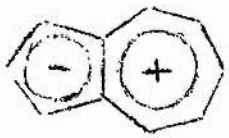
better preparative methods have been devised, and the compounds have thus become more easily available for detailed study.

Azulene, which is isomeric with naphthalene, can be given the Kekule structures XIIIa and XIIIb.

XIII a

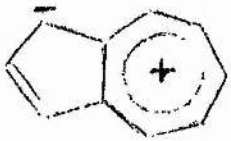
XIII b

It has a dipole moment which is attributed to the tendency of a π-electron to migrate from the seven-to the five-membered ring, to give structure XIV. This structure, in which each of the rings may be considered to have an aromatic sextet of electrons is closely comparable with that of naphthalene.

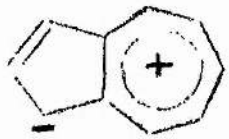


XIV

Stafford and Reid (17) considered azulene to be a resonance hybrid of the two Kekule structures, both of which have a completely conjugated peripheral system, and of XVa and XVb.



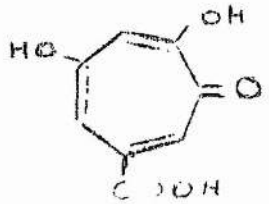
XVa



XVb

Anderson, Nelson and Tazuma (18) have shown that substitution does take place in the 1- position; the formation of an azulenium salt (82) and alkali metal salts (83) may also be noted. The existence of a negative charge on the five-membered ring is also supported by the work of Galloway, Stafford and Reid (19) who carried out uncatalysed Friedel Crafts' reactions with azulene, substitution again being in the 1- position.

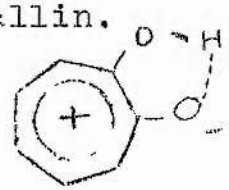
In 1945 Dewar (20) made the first postulation of an aromatic seven membered carbocycle to explain the formula for stipitatic acid, a compound which hitherto had proved impossible to formulate. He suggested the now familiar tropolone structure XVI.



XVI

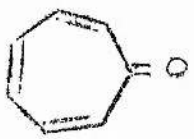
This formulation stimulated work on the tropolones, although the essential nature of the system, i.e. a positively charged seven-membered ring having associated with it an aromatic sextet of π-electrons, was not fully realised until after tropone (XVIIIa and XVIIIb) had been discovered.

The parent compound, tropolone, has been thoroughly investigated by physical methods, which indicate that the C-C double bonds and the carbonyl group are conjugated and that there is intra-molecular hydrogen bonding between the carbonyl and hydroxyl groups. The skeleton is planar, with all the carbon atoms 1.39A apart, the dipole moment is 3.71D and the resonance energy about 36 Kg.cals/mole. The actual structure is a resonance hybrid which may probably best be written as XVII. The tropolones exist in various natural products, including thujaplicins, colchicine and purpurogallin.

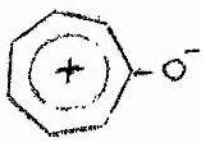


XVII

Tropone may be represented as a resonance hybrid of XVIIIa and XVIIIb.



XVIII a

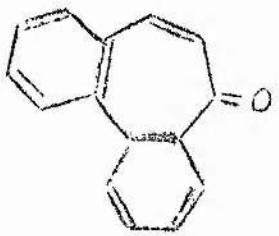


XVIII b

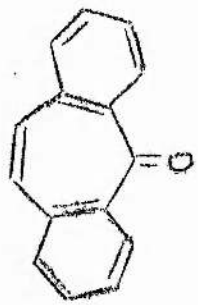
The dipolar structure is supported by the reduction of carbonyl properties, (an instance is the non-formation of phenylhydrazones), a shift in the infra red spectrum, and the high dipole moment (4.3D). Tropone also gives substitution products which further supports an aromatic

structure such as XVIIIb, which is consequent on the polarisation of the carbonyl group. It can, however, be reacted to give an oxime and a semicarbazide under vigorous conditions, showing that there is a contribution from the structure XVIIIa.

4:5-benzotropone shows more or less the same aromaticity as tropone itself, but 2:3-4:5- and 2:3-6:7-dibenzotropones (XIX and XX respectively) show little aromaticity in the seven membered ring, the relevant π-electrons being apparently monopolised by the flanking benzene rings.

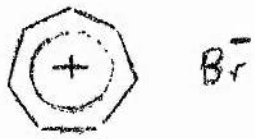


XIX



XX

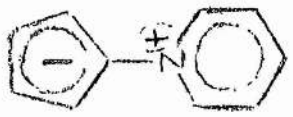
The exocyclic negative charge might be associated with an ion, rather than an atom linked to the ring by a polar bond. A salt of this type had in fact been prepared by Merling (21) in 1891, but its structure was not realised at that time. Doering and Knox (22) repeated Merling's work, and by thermal elimination of hydrogen bromide from the bromination product of cycloheptatriene prepared tropylium bromide, XXI.



XXI

Similarly aromatic stabilisation of a negatively charged five membered ring can be achieved in ionic and dipolar compounds such as XXII and XXIII. Since this provided the theme of the main work of this thesis such compounds are discussed separately in Chapter II.3.

XXII



XXIII

II.2. A simple Molecular Orbital Treatment of Benzene and related molecules.

In benzene the four valency electrons of carbon undergo trigonal hybridisation. This leads to three equivalent orbitals in one plane, directed at 120° to one another. The fourth electron occupies an orbital at right angles to this plane, in the form of two lobes, one above and one below the plane of the other. Three sigma bonds are formed by overlap of the planar orbitals with an orbital from a hydrogen atom and corresponding orbitals from two neighbouring carbon atoms. These sigma bonds form the skeleton of the molecule, and we are left with six π-electrons, each with an atomic orbital of the shape:-

Six molecular orbitals may be constructed by linear combination of these atomic orbitals. It is by consideration of the energies of these molecular orbitals that Hückel's conclusions were evolved (14).

In the Schrödinger equation:-

$$\{H\}\psi = E\psi$$

$\psi = \sum_{r=1}^{6} c_r \phi_r$ and H is the Hamiltonian operator involving only one of the π-electrons. This cannot be expressed explicitly without a knowledge of the wave

functions of all the other electrons, and the important quantities are estimated from experimental findings for one molecule.

Writing out more fully, we have:-

$$\begin{bmatrix} H_{11} & & & & & H_{16} \\ & H_{22} & & & & \\ & & H_{33} & & & \\ & & & H_{44} & & \\ & & & & H_{55} & \\ H_{61} & & & & & H_{66} \end{bmatrix} \begin{bmatrix} c_1\psi_1 \\ c_2\psi_2 \\ \\ \\ \\ c_6\psi_6 \end{bmatrix} = E \begin{bmatrix} c_1\psi_1 \\ \\ \\ \\ \\ c_6\psi_6 \end{bmatrix}$$

from which we obtain six equations of the form

$$H_{11}c_1\psi_1 + \ldots + H_{16}c_6\psi_6 = E\,c_1\psi_1$$

or $$c_1\psi_1(H_{11}-E) \ldots + c_6\psi_6 H_{16} = 0$$

$$c_1\psi_1 H_{21} + c_2\psi_2(H_{22}-E) \ldots + c_6\psi_6 H_{26} = 0 \quad \text{etc}$$

If we discount the trivial solution

$$c_1\psi_1 = c_2\psi_2 \ldots = c_6\psi_6 = 0$$

dividing through by one of $c_r\psi_r$, these give six equations for five unknowns, and the conditions for consistency of these equations may be expressed by:-

$$\begin{vmatrix} H_{11}-E & H_{12} & & & & H_{16} \\ H_{21} & H_{22}-E & H_{23} & & & \\ H_{31} & H_{32} & H_{33}-E & H_{34} & & \\ & & H_{43} & H_{44}-E & H_{45} & \\ & & & H_{54} & H_{55}-E & H_{56} \\ H_{61} & & & & H_{65} & H_{66}-E \end{vmatrix} = 0$$

If we neglect overlap of adjacent orbitals, H_{rr} becomes the energy of one π-electron if restrained to stay on the r th nucleus, with wave function ψ_r, and H_{rs} is the resonance integral which is usually written β_{rs}. If we further neglect all β_{rs} except between neighbours, and give all the non-vanishing integrals the same value β we can ignore all the elements in the determinant except the leading diagonal and off-diagonal elements and the elements in the opposite corners. The terms H_{rr} are also normally taken to be equal with the value E_0, so that our condition for consistency becomes the vanishing of the circulant:-

$$\begin{vmatrix} E_0-E & \beta & & & & \beta \\ \beta & E_0-E & \beta & & & \\ & \beta & E_0-E & \beta & & \\ & & \beta & E_0-E & \beta & \\ & & & \beta & E_0-E & \beta \\ \beta & & & & \beta & E_0-E \end{vmatrix} = 0$$

Rutherford (68) has evolved a method of determining such circulants, so that:-

$$\begin{vmatrix} x & 1 & & & & 1 \\ 1 & x & 1 & & & \\ & 1 & x & 1 & & \\ & & 1 & x & 1 & \\ & & & - & & \\ & & & & - & \\ & & & & & - \\ & & & & x & 1 \\ 1 & & & & 1 & x \end{vmatrix} = 0$$

can be written as the product

$$\prod_{k=1}^{n} (x+2\cos\frac{2\pi K}{n}) = 0,$$

or $(x+2\cos\frac{\pi}{3})\ (x+2\cos\frac{2\pi}{3})\ (x+2\cos\pi)\ (x+2\cos\frac{4\pi}{3})\ (x+2\cos\frac{5\pi}{3})$

$$(x+2\cos 2\pi) = 0.$$

i.e. $(x+1)^2(x-1)^2(x-2)\ (x+2) = 0$

giving six roots.

In our case, to obtain the correct form of the determinant we put $x = \frac{E_0 - E}{\beta}$, dividing each element of the original by β. The values we obtain for E are thus:-

$$E_0+\beta \text{ (twice)} \quad E_0-\beta \text{ (twice)} \quad E_0+2\beta \quad E_0-2\beta .$$

β is negative so that we have three orbitals, given by $E_0+\beta$, and $E_0+2\beta$ whose $E<E_0$ i.e. bonding orbitals. The

other three are antibonding.

The orbitals each hold two electrons with opposing spins and the high resonance stability of benzene is associated with its possession of six electrons which will exactly fill those bonding orbitals.

The approximate value of the energy of the π-electrons from this treatment is $2(E_o+2\beta) + 4(E_o+\beta) = 6E_o+8\beta$. The localisation of each π-electron in the region of bonds in accordance with a Kekule structure would give a total energy of $6(E_o+\beta)$. The difference between these two energy values is 2β, which is the delocalisation energy. A value of 20 Kg.cals/mole has been calculated for β, and the resonance energy thus arrived at agrees quite well with the figures obtained from experiment, and the valence bond treatment.

Clearly we may extend the treatment to a system of n nuclei, and the criterion determining whether a given orbital is bonding or not is whether the term $2\cos 2\frac{\pi k}{n}$ in the factor $x + 2\cos\frac{2\pi k}{n}$ is positive or not.

Cos θ is +ve and non-zero when θ is $< \frac{\pi}{2}$ or $\frac{3\pi}{2}$, so that we get a bonding orbital when:-

$$\frac{2\pi k}{n} < \frac{\pi}{2} \quad \text{or} \quad > \frac{3\pi}{2}$$

$$\text{or} \quad \frac{k}{n} < \frac{1}{4} \quad \text{or} \quad > \frac{3}{4}.$$

Now let n=4m+1, where m=0,1,2,3,-------.

Then $k < \frac{4m+1}{4}$ or $> \frac{3(4m+1)}{4}$.

i.e. $k < m+\frac{1}{4}$ or $> 3m+\frac{3}{4}$

i.e. k may take the values m, m-1, -----3,2,1.

or 3m+1, 3m+2, -------4m+1.

Therefore the number of possible values of k is:-

m+(m+1) = 2m+1,

when n has the values 1,5,9-------.

Similarly, if we express n successively as 4m+2, 4m+3, and 4m+4, we may show that the number of values for k is of the form 2m+1, for all positive values of n. Thus the number of bonding orbitals can also be expressed in this form. As each orbital can hold two electrons, the number of electrons which completely fill these orbitals is 2(2m+1) = 4m+2, which is the Huckel rule for aromaticity (m can take the values 0,1,2,---, and when m=1, we have the particular case of the aromatic sextet as in benzene).

If we take the particular cases of the five and seven membered rings (i.e. n=5 or n=7), it may be seen by inspection that the number of values of k which satisfy the above inequalities is in each case three (i.e. 1,4,5 and 1,6,7 respectively), or the same number as for benzene. Thus there are again three bonding orbitals and stable arrangements will be achieved when these are exactly filled by six electrons.

Extension to heterocyclic molecules.

In a heterocyclic molecule the matrix element H_{rr} and the resonance integral β_{rs} (hetero-atom is r) differ from those in the carbocycles. The difference is not great, and does not affect the general behaviour, although charge distributions can be calculated.

In pyrrole, if all the atoms are hybridised in the trigonal manner, we have two π-electrons on the nitrogen. If the ring is planar these will make up the sextet for the ring, with consequent stabilisation. The lone pair having been used in the resonance, pyrroles do not have the basic properties we associate with such a nitrogenous molecule.

In pyridine the aromatic sextet can be completed without using the lone pair so that it retains its basic properties.

II.3. Aromatic Character in five membered carbon rings.

(a) General Remarks.

The removal of a proton from cyclopentadiene leaves a five membered ring in which the negative charge may be formally placed on each of the carbon atoms in turn to give the five equivalent structures Ia - e.

Ia Ib Ic Id Ie

Resonance is thereby favoured with consequent stabilisation. The five membered ring has now associated with it six electrons and so would be expected to have aromatic properties. Thus, hydrogen from the methylene group in cyclopentadiene would be expected to be somewhat labile.

This is illustrated by the acidity of cyclopentadiene, which is very high for a hydrocarbon, as was indicated by Goss and Ingold (23) in 1928. The resonance energy of the cyclopentadienyl anion has been estimated at 42 Kg.cals/mole by Roberts and his co-workers (24), using the simple molecular orbital theory.

The most widely investigated series of compounds having aromatic character associated with a five membered carbocycle are the ferrocenes and fulvenes.

(b) Ferrocenes.

Ferrocene, or dicyclopentadienyl iron, was first prepared by Kealy and Pauson (25) in an attempt to make fulvalene by the reaction of cyclopentadienyl magnesium bromide with ferric chloride. It has also been prepared by the action of cyclopentadiene on reduced iron in nitrogen at 300°C (89).

Ferrocene is an extremely stable orange solid. It can be sublimed, and does not decompose even on heating to 470°C. It is unaffected by water, acid or alkali even at the boiling point, and can be recrystallised from organic solvents.

The anti-prism structure III was proposed by Woodward (27) and has been proved by X-ray determination of the crystal structure (90). All the C-C bonds are equivalent, as are all the C-H bonds; the C-C bond distance is about 1.4A.

III

Ferrocene behaves as an aromatic compound, resisting reactions such as maleic anhydride addition, and catalytic hydrogenation with Adams' Platinum oxide catalyst, which will reduce benzene rings. Indeed if di-indenyl iron is

subjected to catalytic hydrogenation, the benzene rings are reduced to give di(tetrahydroindenyl) iron (91).

Ferrocene readily undergoes aromatic substitution, particularly Friedel-Crafts acylation. By competition reactions it has been shown that ferrocene is much more reactive than benzene in this respect. Halogenation, nitration and sulphonation reactions are interfered with by oxidation of ferrocene to the positively charged ferricinium ion, which takes place to the exclusion of electrophilic substitution. Sulphonation has been achieved in acetic anhydride.

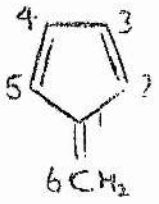
Ferrocenes have been prepared from various substituted cyclopentadienes, the one derived from fluorene being rather unstable. Also the iron may be replaced by other transition metals.

A more complete review of the chemistry of ferrocene and related compounds has been made by Pauson (26).

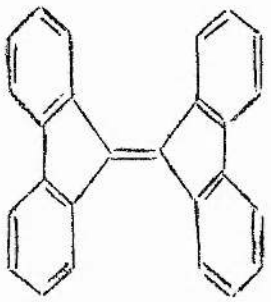
(c) Fulvenes.

The parent compound of the fulvene series, which has not yet been isolated, would have the structure IV. One member of the closely allied fulvalene family, bisdiphenylene ethylene (IVa), has been known since 1875 (28), but the preparation of fulvenes by alkaline condensation

of cyclopentadiene with aldehydes and ketones was first carried out by Thiele (29) in 1900.



IV



IVa

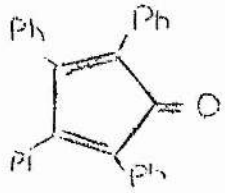
This is the first of the two general methods of preparation. Derivatives of cyclopentadiene vary in their activity under these conditions, so that indene and fluorene are considerably less reactive than cyclopentadiene. This may be attributed to the reduction in symmetry of the ion by annellation. The cyclopentadienyl ion is stabilised by its high symmetry and possession of an aromatic sextet.

Substitution of the olefinic hydrogens also reduces the power of condensation so that phenylated cyclopentadienes react with aldehydes but not with ketones.

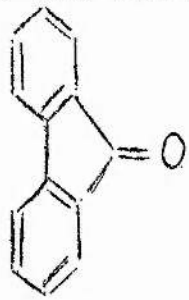
The use of aliphatic aldehydes is of limited applicability as the aldehydes are sensitive to the alkaline reagents, and the resulting monoalkyl fulvenes resinify. However, 6-ethyl fulvene has been obtained pure by this method. The process is frequently complicated by side reactions, and by condensation of a second molecule of

carbonyl compound with the cyclopentadiene.

The second general method of preparation involves the reaction of Grignard reagents, or other suitable organo-metallic compounds, on the so-called fulvene ketones e.g.
2:3:4:5-tetraphenylcyclopentadienone (V) and fluorenone (VI). Dehydration of the tertiary alcohol so formed by chemical or catalytic means yields the fulvene.



V



VI

Fulvenes occur in nature, and also appear in aromatisations e.g. in the oxide catalysed dehydrogenation of hexane, some fulvene is formed as well as benzene.

Much theoretical, and practical, work has been done on the structure of the fulvenes, in particular with regard to bond order, free valency indices and dipole moments; Bergman has published a comprehensive review of this subject (30). The results may be summarised as follows:-

(a) A dipole exists with a direction into the ring.

(b) The cyclic 'double bonds' and the exocyclic bond have reduced double bond character

(c) In general, geometrical isomerism is absent.

The direction of the dipole moment is in harmony with the familiar tendency towards anion formation in the five membered ring. The dipole moment is low compared with that in an ylide such as dimethylsulphonium fluorenylide (which has μ = 6.2D according to Phillips, Hunter and Sutton (31)). This is to be expected as the 6-carbon atom is much less able than sulphur to carry a positive charge.

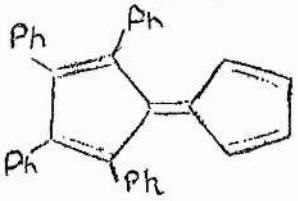
The chemical properties of the fulvenes bear out the ideas of their structure as indicated above. Reduction by lithium aluminium hydride, which is characteristic of a polar double bond such as that in a carbonyl compound, can be effected and in the addition of organo-metallic compounds the alkyl group becomes attached to position 6. A further analogy between the exocyclic double bond and a carbonyl group is the ability of methylene groups attached to the 6-carbon atom to undergo Aldol condensation. In Diels-Alder reactions the fulvenes react variously as dienophiles, dienes or both.

(d) Fulvalenes.

In the related fulvalene series, the simplest member fulvalene (VII) is as yet unknown but the results of molecular orbital calculations indicate that these molecules should be stable. The tendency of both rings to acquire an electron to complete their sextets gives the central bond a low bond order, for a formal double bond, comparable

with that of a benzene double bond. The simplest fulvalene so far obtained is 2:3:4:5-tetraphenyl fulvalene (VIII), an orange-red hydrocarbon, which has been prepared by the action of cyclo pentadienyl magnesium bromide on tetraphenylcyclopentadienone (66).

VII

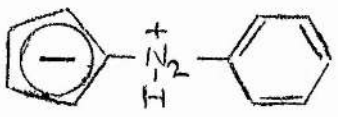


VIII

(c) cycloPentadienylides.

The ionic metal cyclopentadienides have been known for many years, the potassium derivative having been prepared by Thiele (33) in 1901 by the direct action of potassium on cyclopentadiene in benzene solution. The compounds decompose readily, sometimes with explosive violence.

The first dipolar cyclopentadienylide was also in all probability made by Thiele (29). He reported the formation of a quickly resinifying violet coloured substance from the reaction of cyclopentadiene with benzene diazonium chloride in the presence of alcoholic potash. This probably had the structure IX.



IX

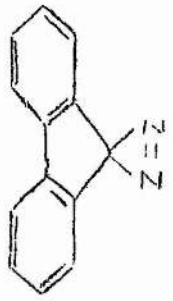
Dibner and Laue (34, 35) continued the investigation, and reported a similar reaction done in the presence of sodium acetate. They were able to crystallise a brown substance (m.p. 130°C) containing 16.83% N ($C_{11}H_{10}N_2$ requires N 16.47%). Roedig and Hornig (36) repeated this work and obtained, in very small quantity, a substance m.p. 115-116°C, which from complete elementary analysis and molecular weight determination they formulated as $C_{20}H_{16}O_2N_4$. They stated that "... as the reaction was certainly not a straightforward one, they were not interested in following it up any further at that time."

The formula $C_{20}H_{16}O_2N_4$ is difficult to derive from a reaction in which the carbon containing units have five and six carbon atoms each, and in view of the difficulties experienced in the present work in obtaining analysis values corresponding well with those expected, perhaps too much reliance should not be placed on them in this instance. The molecular weight figure would fit equally well with a dimer of the simple diazo compound formulated above.

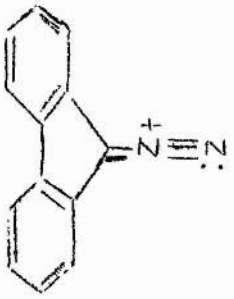
The structures of these diazo derivatives therefore remain in doubt, but in view of Doering's preparation of diazocyclopentadiene (46) it is not improbable that the phenyl derivative may in fact have been formed.

Staudinger and his co-workers (37) describe the preparation of diazofluorene by oxidation of the hydrazone

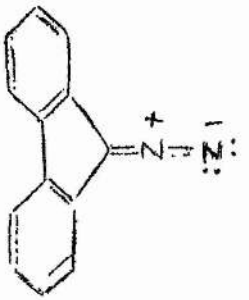
of fluorenone. It was a stable deep red crystalline substance m.p. 94-95°C, for which they gave the structure X; it would now be regarded as a hybrid of structures XI_{a-d}.



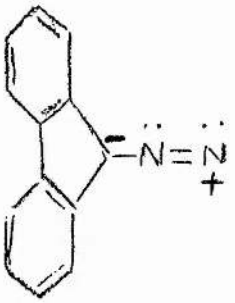
X



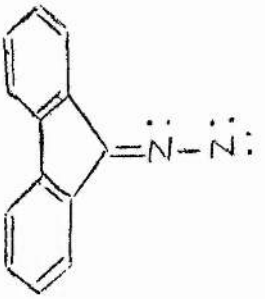
XIa



XIb



XIc

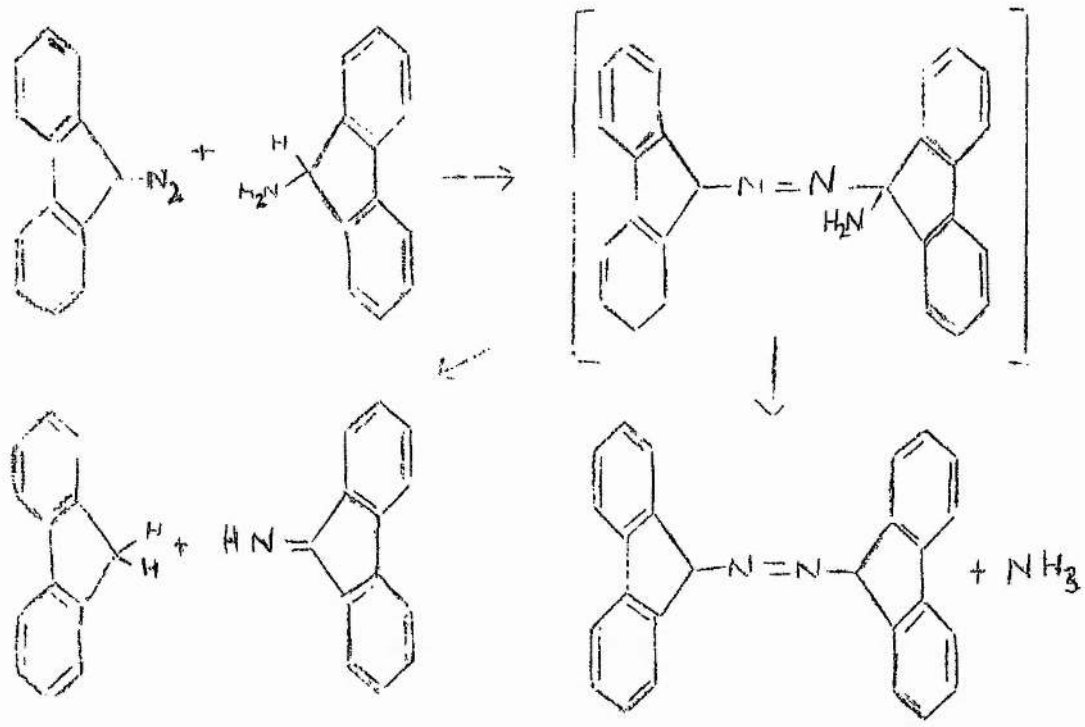


XId

In the forms XIa and XIc the negative charge on the 9-carbon atom gives an aromatic sextet to the five membered ring. Thus this compound should also be regarded as a forerunner of Doering and Depuy's diazocyclopentadiene (46).

Pinck and Hilbert (38) re-investigated diazofluorene, and studied its reactions with various 9-substituted fluorenes. The reaction with 9-aminofluorene to give

a ketazine (XII), or fluorene and fluorylidene amine may thought of as proceeding via an activated intermediate:-

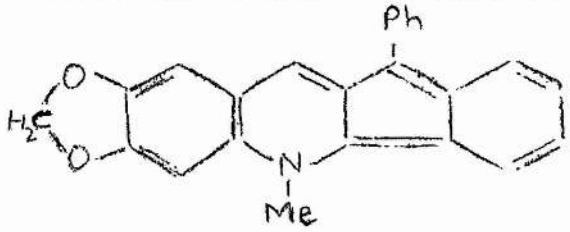


XII

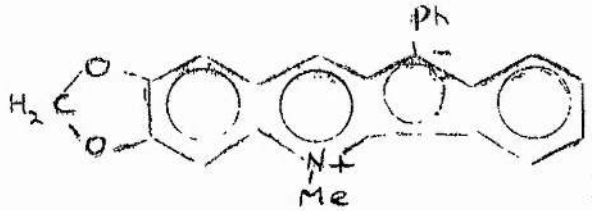
The tendency would be for the 9-hydrogen atom in the aminofluorene to ionise leaving the 9-carbon atom with a negative charge, and the outer nitrogen from diazofluorene would have to be capable of neutralising this charge, which is possible in the case of structure XIc.

Armit and Robinson (13) prepared some anhydronium bases which had five membered rings bearing 6 π-electrons, and a negative charge. Introducing the inscribed circle notation to represent a sextet of electrons, they described one of these as a hybrid with the two structures

XIIIa and XIIIb as extreme forms.

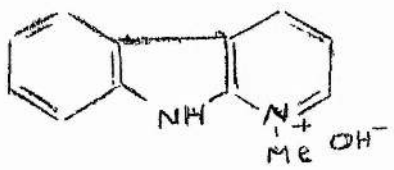


XIIIa

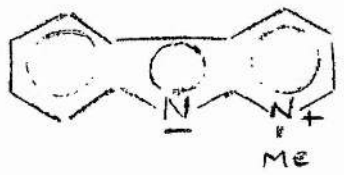


XIIIb

A simpler case is the methohydroxide (XIVa) of 3-carboline which loses water with formation of the anhydronium base XIVb.

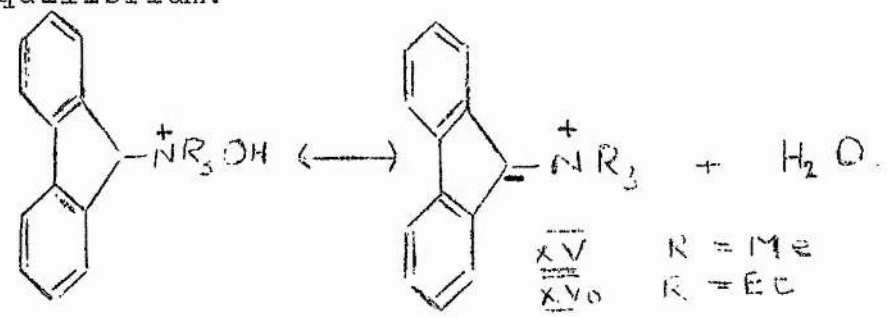


XIVa



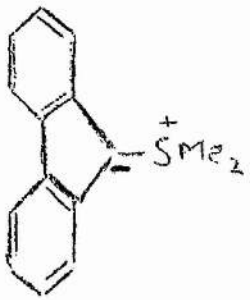
XIVb

Ingold and Jessop (39) prepared fluorenylides by the action of amines and dialkyl sulphides on 9-bromofluorene. In the case of the trimethyl- and triethylammonium 9-fluorenylides (XV) and (XVb), the products were formed in insufficient amount, and were too unstable to isolate, the equilibrium:-

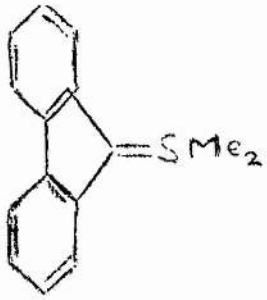


XV R = Me
XVb R = Et

being well over to the left. By analogy with the N-oxides $\bar{O} - \overset{+}{N}R_3$, which have low stability and tend to add water to give hydroxides $(OH\text{-}NR_3{}^{+})\ OH^{-}$, and the sulphoxides $\bar{O} - \overset{+}{S}R_2$ which are more stable and have little tendency to add water, they decided to investigate fluorenyl-sulphonium compounds. The addition of dimethylsulphide to 9-bromofluorene did not take place in ether, benzene or without a solvent, but by applying Richardson and Soper's recently published cohesion principle (40) and carrying out the reaction in nitromethane, the required product was formed in good yield. Treatment with sodium hydroxide yielded a yellow crystalline compound XVIa, m.p. 70°-75°C (Dec.). Phillips, Hunter and Sutton (31) on repeating this work obtained a substance m.p. 126-7°C which decomposed after melting. They ascribed the early decomposition of Ingold and Jessop's product to occluded alkali. The ylide darkens and loses dimethyl sulphide on standing in air, is stable for about 24 hours in vacuo, but decomposes quite rapidly in solution.



XVIa



XVIb

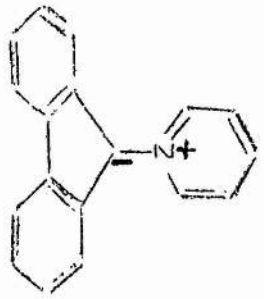
Ingold and Jessop (39) claimed that the trimethyl 9-fluorenylide which they had made, without isolating it, was the first compound to be prepared with a semi-polar bond involving a carbon atom. This claim does not seem to be justified, if the structures suggested above are in fact correct for the diazo compounds prepared about twenty years earlier by Thiele (33) and Staudinger (37).

Phillips, Hunter and Sutton (31) evaluated the dipole moment of dimethyl sulphonium fluorenylide as 6.2D, a much higher value than would be expected from structure XVIb or from either of the two other Kekule structures. Any resonance between these structures involves only the benzene rings and not the molecule as a whole. However, writing the structure with a semi-polar bond the negative charge can be formally placed on any one of the thirteen carbon atoms and the possibilities for resonance are much greater, so that a single bonded structure is stabilised relative to a double bonded one. All thirteen possibilities would have a wide separation of charge and be highly polar.

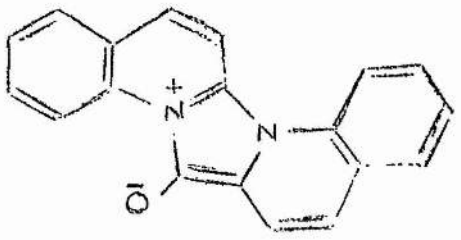
Hughes and Kuriyan (41) suggested that these substances would be stabilised by increasing the positive electrical field over the region of the negative carbon atom. This they did by the introduction of nitro groups into the fluorene nucleus, and prepared dimethylsulphonium -9-(2-nitrofluorenylide) and dimethylsulphonium -9-(2:7-nitrofluorenylide), which were purple crystalline

solids, much more stable than their unsubstituted analogues. On oxidation with chromic acid in glacial acetic acid, the corresponding fluorenone was formed.

The formation of pyridinium-9-fluorenylide (XVII) from fluorenyl-9-pyridinium salts is described by Krollpfeiffer and Schneider (42) in a paper mainly concerned with coloured compounds derived from quinoline and isoquinoline, such as XVIII in which the central glyoxaline ring has an aromatic sextet of electrons. Brief reference only was made to the ylide, and apart from describing its colour, deep blue, no other details are given. Krohnke (43) described enol-betaines involving pyridinium rings, which are highly coloured compounds.



XVII

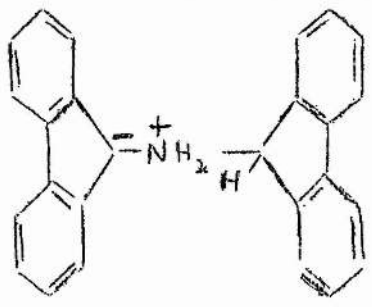


XVIII

In 1946, Pinck and Hilbert (44) prepared pyridinium and α-picolinium fluorenylides by first forming the bromide by the action of the base on 9-bromofluorene. The reactants were allowed to stand at room temperature for several weeks, when the product precipitated from solution. On treatment of an alcoholic solution with alkali, an indigo blue

coloration was formed which faded to green after several hours, then to orange and red. In aqueous solution, addition of alkali gave a purplish blue precipitate, soluble in organic solvents, which decomposed within an hour. A sample treated with liquid ammonia in a sealed tube, remained indigo blue for five days, and then became bluish green. Fluorene and fluorylidene amine were isolated from the reaction mixture.

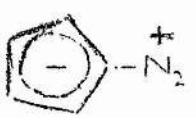
They also reported the preparation of fluorylidene-9-ammonium fluorene (XIX). The hydrobromide of 9:9'-difluorylamine was made from 9-bromofluorene and 9-aminofluorene in acetonitrile, the free base being obtained by boiling the alcoholic solution under reflux. On treatment with liquid ammonia a blue compound was formed, stable in liquid ammonia for six months. The hydrobromide reacted with sodium hydroxide in alcohol at 100° to give a blue coloured compound which faded quickly in air, and more slowly in a sealed tube. In neither case did they attempt to isolate the blue coloured materials.



XIX

Novelli and de Varela (45) prepared pyridinium 2-nitrofluorenylide which was rather more stable, and they obtained it in the solid state. If kept in the dark, and in vacuo, it remained unaltered for at least six months. The solution was stable under the same conditions for several hours, eventually fading to green and then yellow. The m.p. of the substance was described as 'indefinite'.

More recently, in 1953, Doering and Depuy (46) prepared diazocyclopentadiene (XX) by the reaction of cyclopentadienyl lithium on p-toluenesulphonylazide. This is a red liquid, b.p. 52°-53°C at 50 mm, whose structure was proved by analysis and M.W. determination, and by catalytic hydrogenation to give the hydrazone of cyclopentanone which was synthesised independently. The infra red spectrum shows strong absorption at 2082 cm^{-1} (4.80) -- a region generally associated with a triple bond or a system of two cumulated double bonds. Neither of these arrangements is possible in a five-membered ring so the band must be accounted for by the two nitrogens as a diazo grouping. The ultra violet spectrum has a maximum at 298 mμ (logE 4.17) and a long tailing absorption into the visible.



XX

A preliminary notice of the preparation of pyridinium cyclopentadienylide (XXI), as described in later sections of this thesis, was published in 1955 (87).

XXI

Simultaneously with this work, Spooncer (47) synthesised trimethylammoniocyclopentadienylide (XXII) by treating 1:2-bis(trimethylammonio)-3-cyclopentene di-iodide with 40% potassium hydroxide solution under an atmosphere of nitrogen at 80-90°C. One equivalent of trimethylamine was eliminated and identified.

XXII

The ylide was a weak base, pk_b 3.94, which was attributed to the positive inductive effect of the nitrogen, and to the delocalisation of the π-electrons in the five-membered ring. The resonance energy was estimated at 36 Kg.cals/mole. from pH measurements. Chemical evidence suggested that the ylide may undergo one electron loss to form a radical. Derivatives were difficult to prepare, but preliminary investigations suggested that the ylide might undergo aromatic substitution reactions.

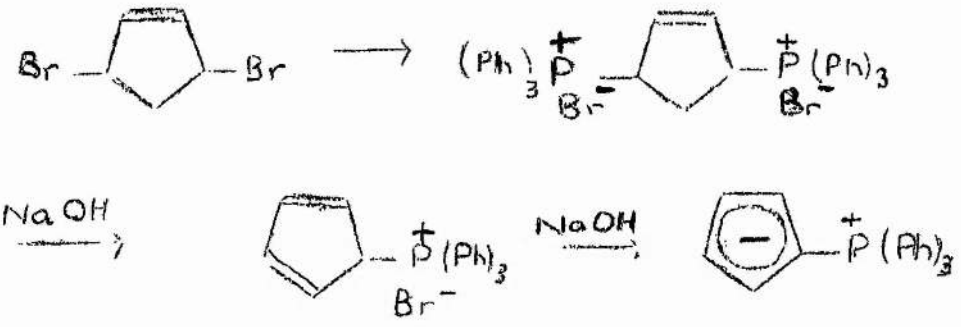
The ylide was a red crystalline solid m.p. ca. 200°C (dec), the formula being proved by elementary analysis, and equivalent weight determination by titration with acid. It was unstable in air and was stored under nitrogen. Hydrogenation with Adams' catalyst in acetic acid yielded cyclopentane and trimethylamine.

Other successful reactions reported were coupling with diazonium salts (in basic solution), bromine absorption in chloroform with the evolution of hydrogen bromide, decolorisation of solutions of iodine, nitric oxide and the formation of intensely blue solutions with chloranil and benzoquinone.

It was soluble, but eventually decomposed in water and polar organic solvents such as chloroform, ethanol, nitrobenzene, acetonitrile and pyridine, with a colour range from red to yellow. It was not soluble in ether, benzene or carbon tetrachloride.

Subsequent to the preliminary publication of the present work (87), Ramirez and Levy (48) reported the preparation of triphenylphosphoniumcyclopentadienylide (XXIII) by the same method as had been used in preparing the pyridinium analogue in this work, i.e. by reaction of triphenylphosphine with dibromocyclopentene in chloroform solution and removal of a proton from the 1-carbon atom with sodium hydroxide.

They gave the reaction sequence as:-



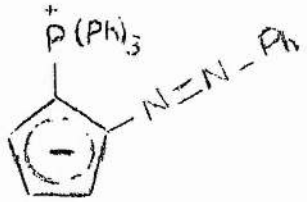
XXIII

No intermediates were isolated, but they indicated that they were intending to investigate these more thoroughly.

The phosphine methylene was a pale yellow crystalline solid m.p. 229-231°C, which could be reprecipitated unchanged from acid solution and was unaffected by prolonged boiling in alcoholic potassium hydroxide solution. No pure picrate was formed from chloroform, benzene or ethanol solution but from carbon disulphide a product m.p. 155°-156°C was formed, which analysed correctly without recrystallisation, as this led to some decomposition. The formula of the ylide was confirmed by elementary analysis, M.W. determination, and hydrogenation in hydrobromic acid solution to give triphenylcyclopentyl phosphonium bromide which was synthesised independently.

The phosphine methylene couples with benzene diazonium chloride in an aqueous methylene chloride system containing sodium acetate (49) to give triphenylphosphonium-

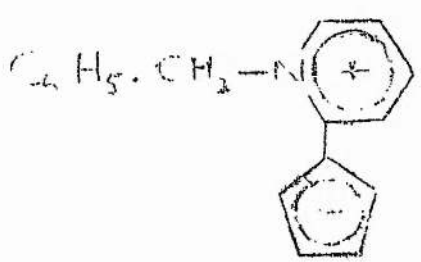
(2-phenylazo) cyclopentadienylide (XXIV) in high yield. This is a deep orange solid m.p. 239-240°C, the structure being proved by elementary analysis, M.W. determination and catalytic hydrogenation of the hydrobromide to give the phenylhydrazone of (2-oxocyclopentyl) triphenylphosphonium bromide, which was synthesised by an alternative route.



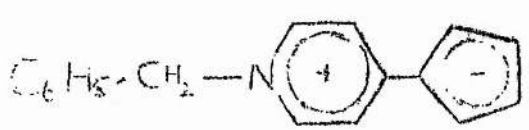
XXIV

The diazo coupling occurs at a position which preserves the cyclopentadienide system and which gives rise to the longest possible conjugated system terminating at the phosphorus atom. The dipole moment of the diazo compound is 6.52D, compared with 6.99D, for the unsubstituted ylide.

In 1957, Kursanov, Baranetskaya and Setkina (50) reported the preparation of a compound XXV by the action of cyclopentadienyl lithium on benzyl pyridinium chloride.

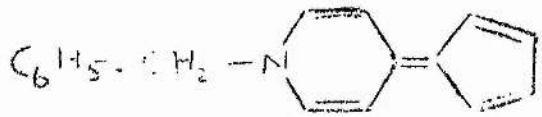


XXV a



XXV b

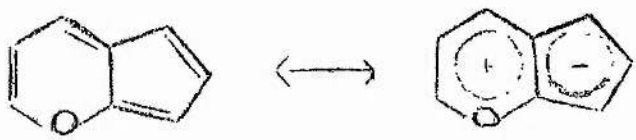
The possibility of a fulvene structure XXVc is discounted because of the very high dipole moment (9.7D) of the molecule.



XXVc

The formula $C_{17}H_{15}N$ for XXV was established, by analysis, M.W. determination, and catalytic hydrogenation to a tertiary amine $C_{17}H_{25}N$.

Also very recently, Boyd (51), has prepared 2-phenyl-benzo(b)cyclopenta(e)pyran and benzo(b)indeno-1:2-(e)pyran by condensation of salicylaldehyde with an appropriate cyclopentanone in the presence of piperidine acetate. The parent system which he wrote:



is an analogue of azulene where -CH:CH- is replaced by -O- .

The two cyclopentapyrans prepared were stable crystalline solids respectively brown-purple and red in colour. The preliminary investigation of the chemical properties and absorption spectra show a resemblance to those of azulene.

III. THEORETICAL SECTION.

1. Introduction.

The present work consisted for the most part of an investigation of the modes of preparation and properties of ylides derived from cyclopentadiene and from 2:3:4:5-tetraphenylcyclopentadiene.

2. Preparation of unphenylated cyclopentadienylides.

The reaction scheme involved in the preparation of these ylides was quite simple. Cyclopentadiene was obtained by de-polymerisation of dicyclopentadiene on distillation through platinum gauze, and brominated in chloroform solution with one molecular equivalent of bromine according to the method of Farmer (52). 1:4-addition is normal, but the orientation and stereo-chemistry of the dibromide were not important for the present work. This dibromide was then treated with two molecules of an organic base. Two possibilities exist for this reaction:-

(i) One molecule of the base removes hydrogen bromide to replace the double bond whilst the other substitutes at the other C-Br position with quaternisation of its nitrogen.

(ii) A di-quaternary salt is formed.

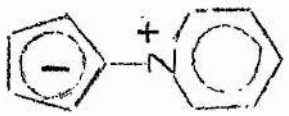
In the first place three organic bases were tried, ammonia, aniline and pyridine. The products from ammonia and aniline were both red in colour, but were difficult to handle and will be discussed later. The possible stabilising effect of delocalisation of the positive charge in pyridine prompted its use as organic base in place of the two other bases mentioned.

The reaction with pyridine, carried out at room temperature in chloroform solution, gave a very dark lower layer. This was separated and the chloroform removed. The residue was found to be very soluble in water; on addition of dilute sodium hydroxide solution a copious precipitate of beautiful red-brown needles was formed which was taken to be pyridinium cyclopentadienylide (I). For proof of structure see below. Although quite stable under nitrogen or if stored in vacuo, these darkened rapidly on exposure to light and air.

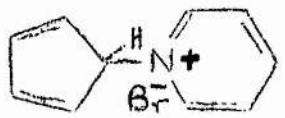
III.3. Structure of the intermediates in the Preparation of cyclopentadienylides.

It was originally thought that the intermediate in this ylide formation was the bromide IIa, and that a crystalline solid noticed in the removal of the chloroform was pyridinium hydrobromide, also produced in this reaction,

i.e. that the reaction had followed the first of the two possible courses mentioned earlier.



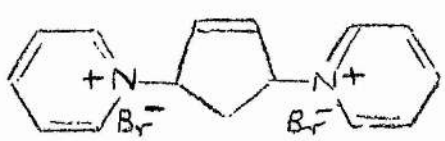
I



IIa

However, several months later more of this reaction mixture was treated with sodium hydroxide with production of the ylide exactly as before. If the intermediate were as above, it seemed surprising that it should have remained stable, standing as it was exposed to the air, and so its structure was reconsidered. At about this time Ramirez and Levy (48) published the preparation of triphenylphosphoniumcyclopentadienylide by an adaptation of the above method. No intermediate was isolated but a tentative reaction scheme suggested that this was a bis(triphenylphosphonium)cyclopentene dibromide.

A compound having the structure IIb would no doubt be more stable than the alternative possibility (IIa) given above, and an attempt was made to isolate and purify the intermediate.



IIb

An earlier attempt to separate it from a supposed mixture with pyridinium hydrobromide by chromatography on alumina had been abandoned as decomposition occurred on the column.

The reaction mixture on standing deposited apparently white or colourless crystals from a black liquor. These were roughly freed from the dark coloured material by pressing on a porous plate or between filter papers. The light brown solid, m.p. 200°C, could be recrystallised from ethanol or methanol (being insoluble in non hydroxylic solvents), but discoloration usually occurred on heating. A better product was obtained by chromatography on a neutral medium, filter cel being used.

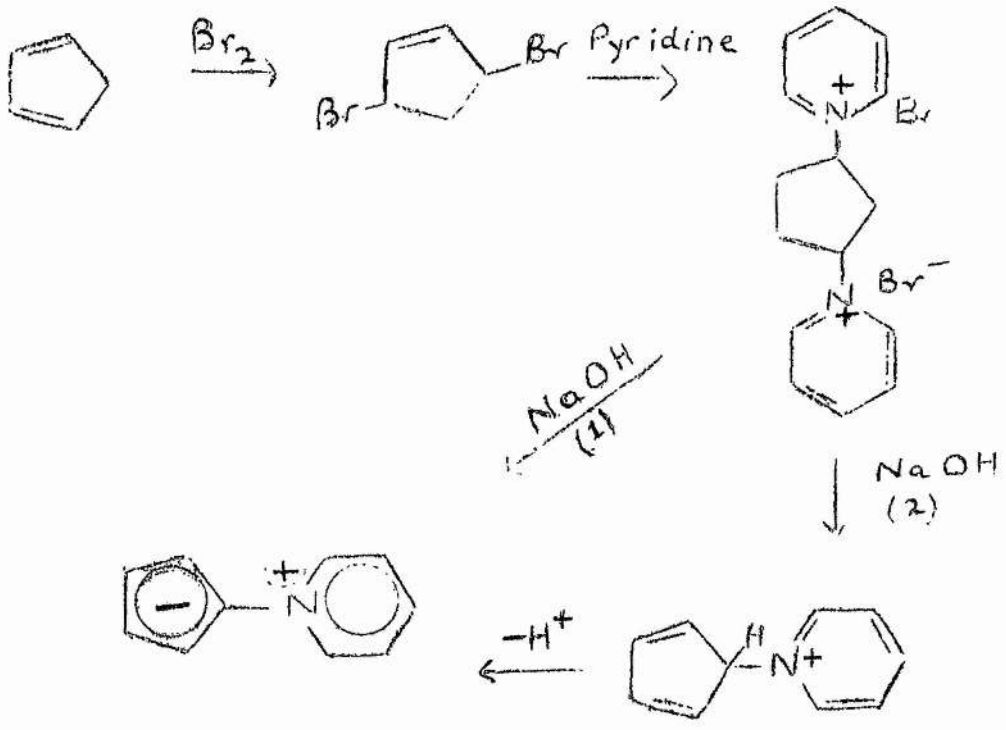
Analysis of this product was inconclusive, and difficulty in getting satisfactory analysis results was encountered throughout this work. A discussion of this and possible causes is included in Appendix II.

Addition of bromine in alcoholic solution to purified samples of the intermediate, also dissolved in alcohol, was carried out and the product analysed. Here a very high bromine figure suggested that the material was contaminated with occluded bromine, as the total of analysis figures added up almost exactly to 100%. Thw addition was checked quantitatively by addition of a known excess of bromine solution, filtration of the product,

and weighing. The bromine in the filtrate was back titrated by liberating iodine from potassium iodide and titrating conductometrically with standard thiosulphate solution. The yield of brominated product showed an increase in weight slightly less than that for one double bond. The back titration indicated that almost exactly one molar equivalent of bromine had been taken up. These results support a formula containing one rather than two double bond per molecule, which favours structure IIb.

A picrate was prepared from the intermediate, and this was a stable yellow crystalline solid m.p. 192°C, in contrast with the picrate formed with considerable difficulty from the ylide itself. This latter was a brown solid which decomposed with some sign of melting at about 95°C. The picrate from the ylide would be expected to be the same as one formed from IIa, indicating at least that this were not the correct structure of the intermediate. Analysis of the first mentioned picrate was inconclusive but the corresponding intermediates in experiments using γ-picoline and dimethyl sulphide gave picrates analysing correctly for a structure analagous to IIb, thus confirming the latter to be the correct formulation for the intermediate.

The reaction scheme may thus now be written:-



where the alternative routes (1) and (2) probably amount to the same thing.

Some further confirmation derived from the fact that on treatment even of a purified sample of the intermediate with sodium hydroxide, the presence of pyridine was detected by smell.

A reaction set up when only one equivalent of pyridine was used, gave a different product on treatment with alkali. It was a dark coloured solid, giving a blood red colour in solution, and still contained bromine. Again analysis gave no conclusive evidence. A picrate was prepared but

could not be recrystallised as it decomposed on heating. An analysis sample of the picrate was therefore prepared by filtering a hot solution of the compound and precipitating the picrate with a filtered alcoholic solution of picric acid but the analysis was inconclusive.

III.4. Proof of the structure of pyridinium cyclopentadienylide.

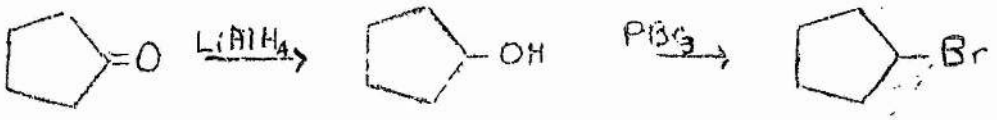
Satisfactory analysis results on the ylide could not be obtained, although the C:H ratio was approximately correct. (For a discussion of this see Appendix II).

Attempts at the preparation of a methiodide, trinitrobenzene adduct or picrate under normal conditions did not give tractable derivatives, but a picrate was obtained in the cold.

Catalytic hydrogenation in alcoholic solution with Adams' platinum oxide catalyst was carried out. The hydrogen uptake corresponded to approximately five equivalents, that is to say complete hydrogenation. The product proved to be N-cyclopentylpiperidine, which had previously been prepared by Loevenich, Utsch, Moldrickx and Schaefer (53) from the reaction of bromocyclopentane with piperidine.

Bromocyclopentane was prepared from cyclopentanone by reduction with lithium aluminium hydride and treatment

of the resulting alcohol with phosphorous tribromide. Thence an authentic sample of N-cyclopentylpiperidine was prepared.



The identity of the two substances was proved by melting point and mixed melting point of their picrates and oxalates, and in this case analysis of the picrate also gave the required figures.

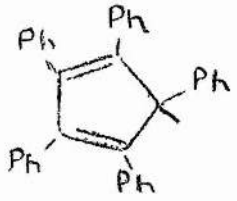
Attempts were made to confirm the structure by an equivalent weight determination by titration with dilute hydrochloric acid. However, the colour of the solutions made the use of indicators difficult and an electromeric titration using an automatic titrimeter was unsuccessful. The results obtained did, however, agree approximately with the formula $C_{10}H_9N$.

III.5. Investigation of the possible formation of other cyclopentadienylides.

A tolerably stable ylide having been prepared by the simple method described above, it was sought to make other compounds of the same type; three methods were used.

In the first, the reactivity of a variety of organic bases with dibromocyclopentene was tested under conditions similar to those used with pyridine.

The existence of a stable free radical 1:2:3:4:5-pentaphenylcyclopentadienyl, (III), (54) suggested that stable cyclopentadienylides might be derived from tetraphenylcyclopentadiene; it would in any case be interesting to examine the effect of substitution in the five-membered ring on the stability of these ylides.



III

The third variation involved the association of the exocyclic positive charge with an element other than nitrogen. Thus the preparation of sulphonium analogues was attempted (cf. Ingold and Jessop's dimethylsulphonium fluorenylide (39)), and the possibility of making a pyrylium ylide was also investigated. In the event of the pyrylium ylide being obtained a diverting possibility appeared. This was that

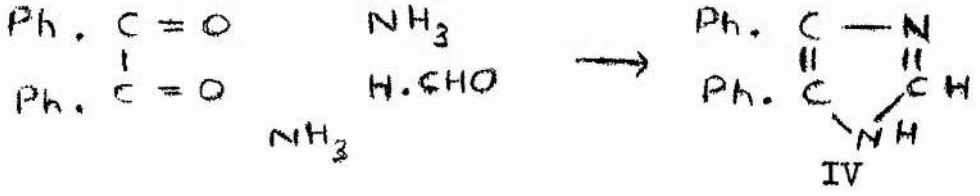
on treatment with ammonia the derivative should give rise to a pyridinium compound, which would be an isomer of the original pyridinium ylide. The preparation of a compound of this type was later reported by Kursanov et al (50), although a different method was used.

III.6. The Use of Different Organic Bases.

The reaction of several different bases with dibromocyclopentene was investigated. In most cases the bases were cyclic, but hydrazine was also used. In this last case it was hoped to be able to prepare a compound which could be oxidised to diazo cyclopentadiene so providing a rather simpler route to the latter compound than that of Doering and Depuy.

As three of the bases had to be synthesised, outlines of the methods employed will be mentioned first. In each case the examples of a given ring type were chosen with a view to ease of preparation, and it was not considered worthwhile to attempt the preparation of less highly substituted derivatives.

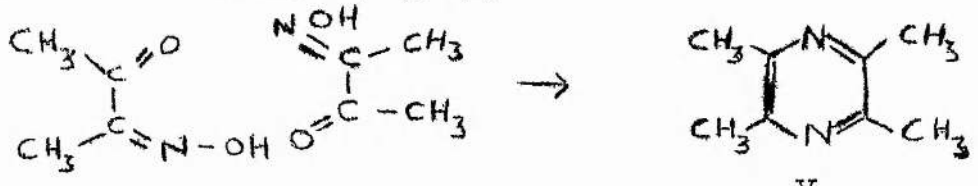
4:5 diphenyl glyoxaline. (IV) This was an example of a glyoxaline which appeared most convenient of preparation. The method of Davidson, Weiss and Jelling (55) was followed. This involved the condensation of benzil with ammonia and formaldehyde.



IV

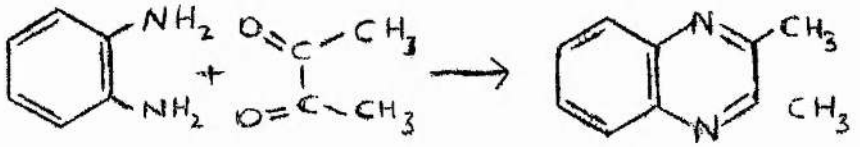
Hexamethylene tetramine acts as the source of both ammonia and formaldehyde. The reaction was carried out in glacial acetic acid, and gave a good yield of an easily crystallised product.

Tetramethylpyrazine. (V) This was prepared by the reduction of diacetyl monoxime with stannous chloride and hydrochloric acid, followed by neutralisation and treatment with mercuric chloride. (56).



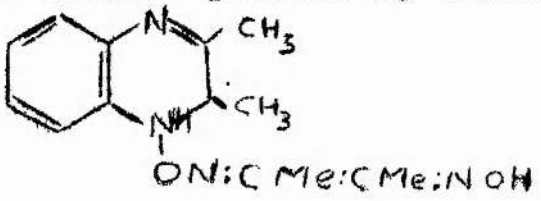
V

2:3-dimethylquinoxaline (VI) In a sodium acetate acetic acid buffer solution, o-phenylenediamine condenses with diacetyl or diacetyl monoxime to give a good yield of crystalline product (57). With diacetyl the quinoxaline is formed directly:-



VI

The oxime first gives a compound (VII) which may be converted into the desired product by alkali.



VII

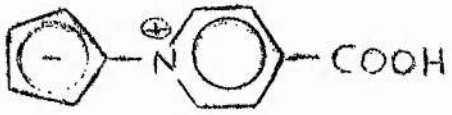
5:7-dimethyl-2:3-benzo-1:4-diazepine. A sample of this diazepine was provided by D.R. Marshall, of St. Andrews University, who had prepared it according to the method of Haley and Maitland (58).

The reactions of these, and other bases, with dibromocyclopentene were tested under more or less standard conditions. A bulk solution of dibromocyclopentene was prepared and stored in the refrigerator. The calculated amount was provided in each case by using a measured volume of the chloroform solution.

The reactions were in general carried out at room temperature in chloroform solution, and after mixing, the organic base and the dibromocyclopentene solution were allowed to stand for at least twenty-four hours. After removal of the chloroform the residue was extracted with water, or dilute hydrochloric acid, and the extract made alkaline with sodium hydroxide solution. The criterion of ylide formation was taken as the formation of a coloured precipitate, or, failing that, the coloration of a chloroform layer on shaking with the alkaline solution.

The results in practically all the cases tried were disappointing and are summarised in Table I. The substituted pyridines were successful in some measure however, and γ-picoline gave an ylide exactly comparable with that from pyridine. It differed very slightly in colour, and resisted catalytic hydrogenation even with freshly prepared Adams' platinic oxide catalyst.

In considering possible products of oxidation of γ-picolinium cyclopentadienylide, the formation of one with the structure VIII would indicate that the cyclopentadienyl ring were more stable to oxidation than a methyl side-chain.



VIII

The preparation of this compound was therefore attempted from isonicotinic acid, and a reaction between dibromocyclopentene and isonicotinic acid was set up. It was also, however, not successful.

TABLE I.

Attempted Reactions between Heterocyclic Bases and Dibromocyclopentene.

Base.	Conditions.	Treatment of product.	Result.	Conclusion as to ylide formation.
4:5-diphenyl glyoxaline.	Refluxed in alcohol for several days		No coloured material.	Difficulty of quaternising glyoxaline prevented possible ylide formation.
2:3-dimethyl quinoxaline	Room temp. in $CHCl_3$ overnight.	Solvent removed. Extract. with water and added NaOH	Slightly pink soln. and white pptate. Blue colour in acid.	Inconclusive, small amounts of coloured materials only involved. Picrate prepared proved to be that of 2:3-dimethyl quinoxaline.
5:7-dimethyl-2:3-benzo-1:4-diazepine.	Room temp. in $CHCl_3$ over weekend.	Dark coloured deposit filtered off. Strong red of diazepine cation. All attempts to separate from any other product failed.		Appearance of strongly coloured by-product prevented thorough investigation.
Tetramethyl-pyrazine (hydrate)	Room temp. in $CHCl_3$, several days.	Chloroform soln. shaken with H_2O and HCl-no extraction of coloured material to aqueous layer.	No coloured product on treatment with sodium hydroxide.	No ylide formed.
Quinoline.	Room temp. in $CHCl_3$, several days.	Acid extraction made alkaline with NaOH.	Trace of pink coloration.	Inconclusive.
Hydrazine hydrate.	Room temp. in $CHCl_3$, overnight.	Two layers (both coloured red) Separated. Treatment with acid or alkali little effect.	Removal of $CHCl_3$ from lower layer gave red non-cryst. material unstable to heat.	Inconclusive.

TABLE I (continued).

Base.	Conditions.	Treatment of product.	Result.	Conclusion.
α-picoline	Room temp. in $CHCl_3$ overnight or for a prolonged period.	Chloroform removed, extracted with water and NaOH solution added.	Red pptate. with 40% NaOH	Some ylide formation.
β-picoline			Red pptate. with dil. NaOH	Ylide formation.
γ-picoline			Red pptate. with 40% NaOH	Some ylide formation.
2:6-lutidine			Ditto (smaller amount).	
2:4:6-collidine			No coloured products.	No ylide formed.
Trimethylamine				
Triethylamine				
Isonicotinic acid.				

Reaction of dibromocyclopentene with Ammonia and Aniline.

The first attempts at the preparation of ylides in the present work were made using ammonia and aniline as the nitrogenous bases. Although coloured products were obtained in each case their instability made them very difficult to work with, and less time was devoted to their study.

Reaction with Ammonia.

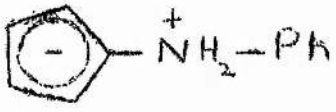
Dibromocyclopentene was prepared in the usual manner, the chloroform being removed under reduced pressure. A slight excess of .880 ammonia solution was shaken with the bromo compound in a stoppered flask. There was no immediate reaction, but after about thirty minutes sufficient pressure was built up to eject the stopper. The reaction mixture was red, with some tarry material sticking to the walls of the flask. The mixture was extracted with water, giving a red solution and leaving the tar undissolved. No coloured material from the aqueous solution was extracted into ether, chloroform or benzene, but some extraction was achieved with methylene dichloride. Evaporation of the solvent left a red gum which was very sensitive to heat, and no longer soluble in water. An alcoholic solution, on treatment with picric acid solution, gave a yellow precipitate which darkened rapidly.

A chloroform solution of dibromocyclopentene was allowed to stand overnight with liquid ammonia. When the

ammonia had evaporated, the residue contained no coloured material, nor did it show any reaction with sodium hydroxide solution.

Aniline.

Dibromocyclopentene was allowed to react with aniline at about -10°C. The resultant sludge was extracted with chloroform, the red solution evaporated under reduced pressure and finally in a vacuum desiccator. A 'puffy', plastic-like product was obtained which could be crumbled to a light brown-red solid. This material was sensitive to heat, and recrystallisation was made almost impossible as a result. The colour of its solution was discharged by acid and restored by alkali. Analysis did not correspond with a simple formula such as IX, and no tractable derivatives were obtained.



IX

Catalytic hydrogenation was inconclusive. The hydrogenation product did not give the same derivatives as an authentic sample of N-cyclopentylaniline, prepared by the method of Loevenich et al, (53). Acetylation of the reduction product gave a solid which did not depress the melting point of a sample of acetanilide. It may be noted that Spooncer (47) obtained trimethylamine on

catalytic hydrogenation of trimethylammonium cyclopentadienylide.

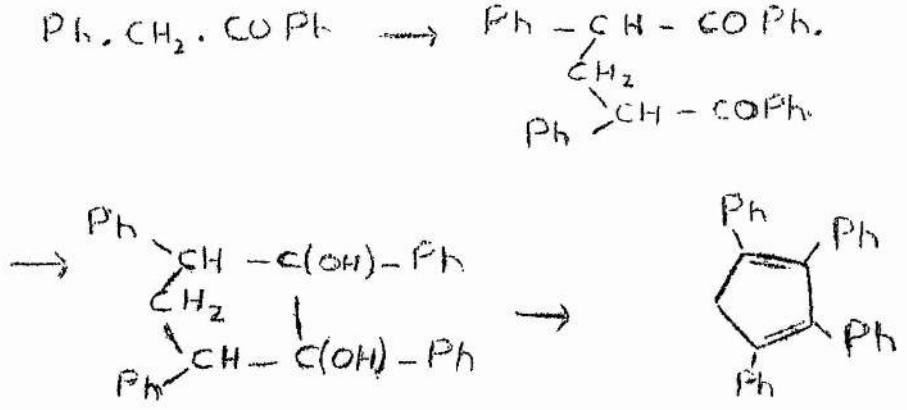
The structure of the brown red substance remains in doubt.

III.7. Alternative sources of the five-membered ring.

A method for the preparation of phenylated cyclopentadienylides seemed possible by the reaction of pyridine, or other bases, with 1-bromo-2:3:4:5-tetraphenylcyclopentadiene, and other similar phenylated cyclopentadienes. The formation of indenylides was also briefly investigated.

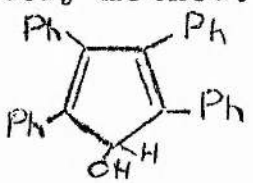
2:3:4:5-Tetraphenylcyclopentadiene (VIII).

In the paper reporting the preparation of the stable free radical pentaphenylcyclopentadienyl, Ziegler and Schnell (54) gave a method for the preparation of 2:3:4:5-tetraphenylcyclopentadiene (VIII). This consists of the condensation of desoxybenzoin with formaldehyde in methanolic caustic potash solution to give methylene bisdesoxybenzoin, which was ring closed by reduction with zinc and acetic acid. The resultant diol was dehydrated by concentrated sulphuric acid in boiling glacial acetic acid. Desoxybenzoin was made by reduction of benzoin with zinc dust in boiling acetic acid, or by a Friedel Crafts' reaction with phenylacetyl chloride and benzene.



VIII

The hydrocarbon (VIII) had been brominated in the 1-position by Kainer (59), using N-bromo-succinimide in carbon tetrachloride. An alternative preparative route for this bromo compound was also investigated. As tetraphenylcyclopentadienone can be very easily prepared from benzil and dibenzyl ketone (60) it was used as starting material. The reduction of this ketone has been studied (61), but no satisfactory reaction has been found to yield tetraphenylcyclopentadiene. Reverse reduction with lithium aluminium hydride gives the rather unstable alcohol (IX) and it was thought that treatment of this alcohol with phosphorus tribromide might yield the 1-bromo compound. No tractable solid was obtained in this way, and no more work was done in this direction as it seemed that it was in fact a less satisfactory method.



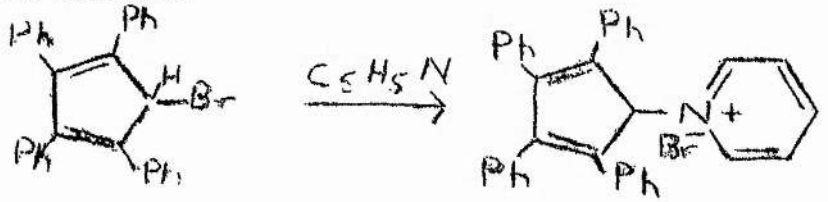
IX

Formation of ylides from 1-bromo-2:3:4:5-tetraphenyl cyclopentadiene.

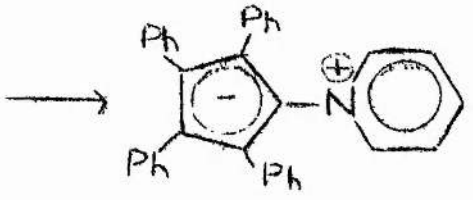
In general the bromo compound was allowed to react with an excess of the organic base at room temperature for at least twenty-four hours. The quaternary salt, e.g. X, usually crystallised out, and was filtered off and freed from base by washing with hexane or petroleum ether.

These bromides could normally be re-crystallised from alcohol and are quite insoluble in water.

The elements of hydrogen bromide could be removed very easily. Although the salt does not react with sodium hydroxide in aqueous solution, a blue-purple coloration was obtained on addition of a little alcohol or acetone to an aqueous suspension of the bromide. Acceleration of this reaction is naturally achieved by addition of sodium hydroxide solution, whereat a crystalline precipitate of the dark blue coloured ylide, e.g. XI, is obtained:-



X



XI

These ylides appear to be completely stable in the solid state, but in solution they decompose quite rapidly. Their solutions vary in colour with the polarity of the solvent, being red in alcohol and blue in benzene and ether.

The liquors after separation of the salt were diluted with water and a dark brown solid was precipitated. This was shown to be tetraphenylcyclopentadienone by means of the melting points and mixed melting points of the two,

and of their maleic anhydride adducts. The most simple, but rather unlikely, explanation was that in the reaction with N-bromosuccinimide some dibromo derivative had been formed, and that this had been hydrolysed to give tetraphenylcyclopentadienone. However this idea had to be discarded as the original bromo compound showed no reaction on standing in aqueous, or aqueous alcoholic solution even in the presence of sodium hydroxide. The formation of tetraphenylcyclopentadienone might otherwise have been caused by hydrolysis of the salt followed by atmospheric oxidation.

The relative ease of separation of an intermediate made the course of these reactions much easier to follow. The ylides themselves proved very difficult of recrystallisation, but the salts caused no such problems and thus a reasonably pure final product could be obtained. As before, satisfactory analyses were very difficult to obtain, carbon and hydrogen rarely giving the anticipated figures. A reasonable correspondence was got for nitrogen, and in the case of the salt, also for bromine.

A similar range of organic bases as before was reacted and the results obtained followed the same general pattern. α-Picoline gave a very much smaller yield, and 2:6-lutidine a negligible amount of coloured material. In fact, in the latter case the hydrobromide of the base was

the principal product. The low reactivity in these instances may presumably be attributed to steric inhibition caused by the α-methyl groups.

The quinolines gave better evidence of ylide formation. In the case of quinoline itself no salt crystallised even after three or four months, even on addition of petroleum ether. However, an alcoholic solution of the reaction mixture gave a blue precipitate on making alkaline.

4:5-diphenylglyoxaline and 5:7-dimethyl-2:3-benzodiazepine both failed to give any evidence of reacting with the 1-bromo-2:3:4:5-tetraphenylcyclopentadiene even on refluxing in nitromethane-benzene mixtures.

Picrates could be prepared either from the quaternary salts or the ylides. These were, as anticipated, identical and gave more satisfactory analysis.

The results obtained are summarised in Table II.

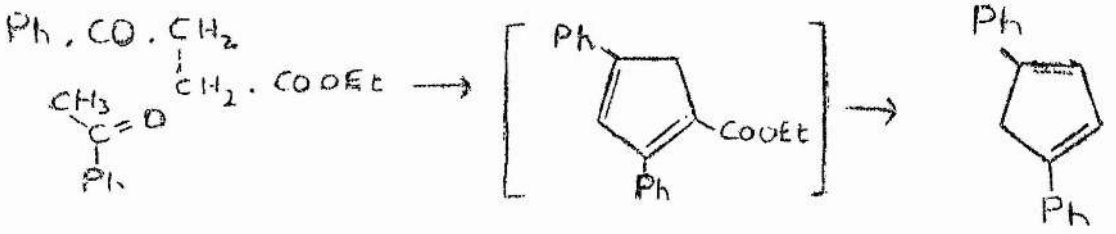
TABLE II.

Attempted Reactions between Heterocyclic Bases and 1-Bromo-2:3:4:5-tetraphenyl-cyclopentadiene.

Base.	Conditions.	Intermediate.	Result on treatment with NaOH.	Conclusion as to ylide formation.
Pyridine β-picoline γ-picoline	Allowed to stand together for 1-2 days. Base in excess.	Crystalline. fair to good yield.	Crystalline dark blue or purple solid	Ylide formation.
α-picoline	3 days standing; base in excess.	Low yield of crystalline material.	Dark red-purple solid obtained.	Ylide formation greatly inhibited by α-substitution.
2:6-lutidine	3 days standing; base in excess.	Moderate yield of crystalline material, mostly hydrobromide of 2:6-lutidine.	Some blue-purple coloration.	Very small amount of quaternary salt formed, which does give an ylide as before.
Isoquinoline.	10 days standing in a few ccs. benzene. approx. calc. amount of base.	Low yield of cryst. material. Picrate proves to be that of isoquinoline.	Blue solid formed which faded on standing under water.	Small amount of intermediate formed which does yield an ylide.
Quinoline.	Base in excess. 3 months standing.	No crystalline material.	Blue solid obtained.	Ylide formation.
4:5-diphenyl-glyoxaline.	First standing, then refluxing of calculated amount in benzene/nitromethane solution.	Removal of solvents gave only starting material.		Nil.
5:7 dimethyl-2:3-benzodiazepine.				Nil.

Other phenylated cyclopentadienes.

2:5-diphenylcyclopentadiene was prepared by condensing ethyl β-benzoylpropionate with acetophenone in dry benzene in the presence of sodium ethoxide (62).



XII

Bromination with N-bromosuccinimide did not give the desired product; possibly the free radical nature of the reaction caused polymerisation to set in. Addition of one molecule of bromine to this compound was attempted, but no promising results were obtained.

The preparation of 3:4-diphenylcyclopentadiene was attempted from dibenzoylpropane, which was itself synthesised via ethyl benzoylacetate and ethyl dibenzoylglutarate (63). The final steps were to have been pinacone reduction of this diketone and dehydration of the resultant cyclic diol. Various methods of pinacone ring closure were used without success. Other workers (64) have also reported difficulty with this and related ring closures. The most convenient method available appeared to be the use of zinc in boiling acetic acid, and this was more thoroughly investigated. However, despite

rigorous purification of the acetic acid and the use of a variety of different grades of zinc, no diol was obtained. The diol has been prepared by Japp and Michie (63), although by a rather lengthy method involving the use of aluminium amalgam in wet ethanol, and this matter may be further investigated.

Indene.

A comparison of stability between fluorenylides, indenylides and cyclopentadienylides was obtained by making an indenylide from 1-bromoindene (cf.86), prepared from indene by reaction with N-bromosuccinimide. On treatment of the bromoindene with pyridine a deep red solution was obtained; addition of alkali gave a dark blue material which when extracted into chloroform imparted a blue coloration to the solution. The solid darkened rapidly, and the colour of the solution faded in a few minutes.

Thus pyridinium indenylide is less stable than the cyclopentadienylide, and of about the same stability as the fluorenylide. The comparative instability of indene itself indicates that the 2:3 bond can be thought of as an isolated double bond, and the lower acidity compared with cyclopentadiene is attributed to the relatively smaller increase in resonance energy of the molecule in forming an ion, there already being substantial resonance energy from the benzene nucleus. Indene is more acidic than fluorene,

and as this is about the only physical measurement which can be usefully applied to the prediction of stability of compounds such as ylides, we might expect the indenylides to be more stable than fluorenylides. It is difficult to find a satisfactory reference standard in such matters, and in any case the increased molecular weight of the fluorene compounds might bestow additional stability sufficient to account for any resonance differences.

III.8. Attempted preparation of ylides in which the positive charge is associated with atoms other than nitrogen. Sulphur.

Ingold and Jessop found that the dimethylsulphonium fluorenylide was considerably more stable than the trimethyl ammonium derivative (39), so it was decided to attempt the preparation of the corresponding cyclopentadienyl derivatives.

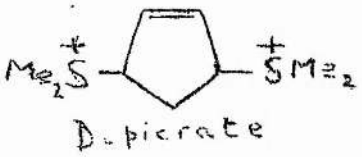
Diphenyl sulphide, in keeping with its reluctance to form sulphonium salts, did not react with 1-bromo-2:3:4:5-tetraphenylcyclopentadiene even in boiling nitromethane.

Dimethyl sulphide was allowed to stand with 1-bromo-2:3:4:5-tetraphenylcyclopentadiene in (a) benzene solution (b) a mixture of nitromethane and benzene, for about two months. Little reaction appeared to have taken place although the solution became slightly red in colour.

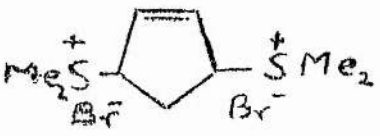
Alkaline treatment of samples of the reaction products did not, in either case, yield any coloured products. On removal of the solvents from the reaction mixtures a dark solid was obtained, which was proved to be tetraphenylcyclopentadienone by melting point and mixed melting point determination.

More promising results were obtained by allowing dimethyl sulphide to react with dibromocyclopentene in chloroform solution. After standing overnight a viscous

brown material was obtained, which could not be crystallised. A picrate was prepared, and this analysed correctly for XIIIa, indicating that the intermediate XIIIb had been formed.

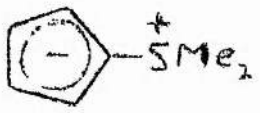


XIIIa



XIIIb

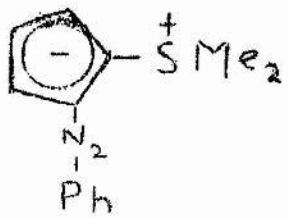
Alkaline treatment of the intermediate, but not of the picrate, yielded a red-brown oily precipitate. This was taken up in chloroform, and on removal of the solvent a red-brown solid product was obtained. This gave a brown-yellow colour in solution, the shade varying slightly with the polarity of the solvent. This product was assumed to be dimethyl sulphonium cyclopentadienylide (XIV), although a satisfactory elementary analysis could not be obtained.



XIV

On treatment of XIV with benzene diazonium chloride, a dark red precipitate was obtained which dissolved in organic solvents to give red solutions. Again analysis did not correspond well with a simple product such as

XV. (cf. (49)).

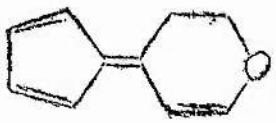


XV

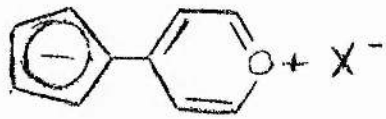
No tractable picrate was obtained from either the ylide or the diazo compound. The ylide however, gave a deep blue solution with chloranil, which faded slowly on standing.

Oxygen.

The projected pyrylium ylide formation involved, in effect, making a fulvene (XVI), and then making its salt (XVII) by treatment with acid.



XVI

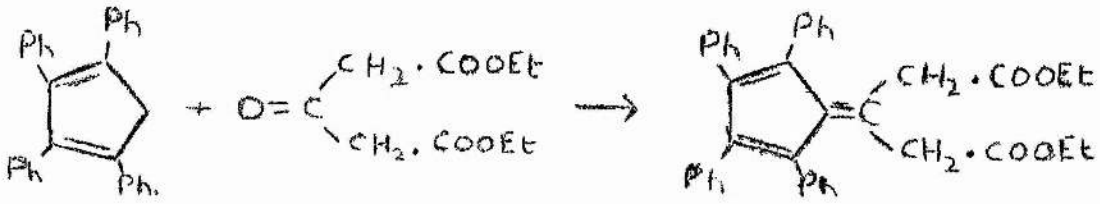


XVII

For the sake of having intermediates which would be expected to be more stable and easy to handle, a substituted cyclopentadienyl compound was used. Two routes were considered, namely to condense with the diene a substance suitable for ring closure to a pyrylium salt, or to react a Grignard reagent from the diene with a γ-pyrone.

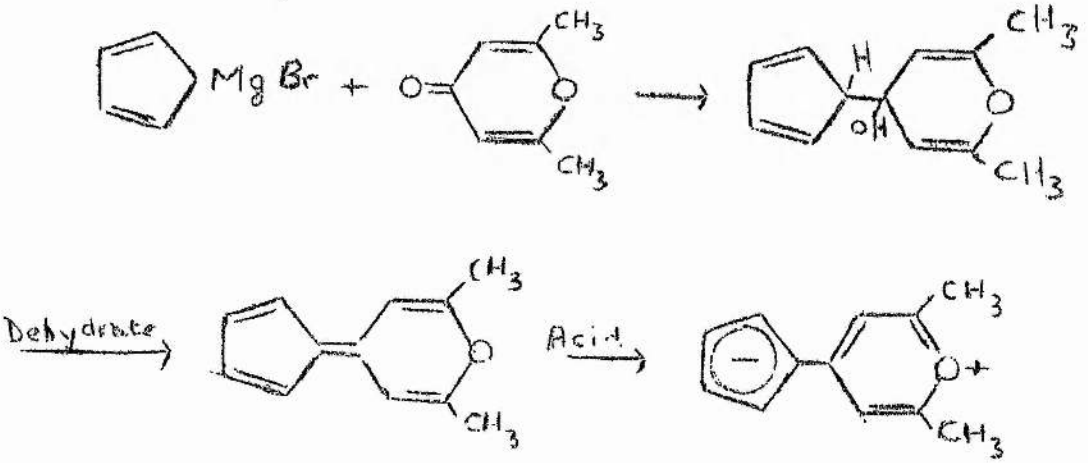
Acetone dicarboxylic ester would be possible reactant in the first route and a reaction scheme was envisaged as

follows, with subsequent ring closure by heating with hydrochloric acid:-



This was not followed up at the time, as 2:6-dimethyl γ-pyrone was more easily accessible than acetone dicarboxylic ester. It was prepared by heating dehydroacetic acid with concentrated hydrochloric acid.

Although carbonyl activity is considerably reduced in γ-pyrones, Baeyer and Piccard (65) record the reaction of 2:6-dimethyl-γ-pyrone with methyl magnesium bromide, so that it was hoped to employ one of the general methods of fulvene formation, using a cyclopentadienyl magnesium bromide:-



In acid solution there would be the conflicting tendency of the five-membered ring to take up a proton, and the acidity would obviously need careful control.

Pauson (64, 69) attempted the preparation of tetraphenylcyclopentadienyl magnesium bromide, apparently without success, but had better evidence for the formation of the lithium derivative. Weinmayr (88), also investigating arylated ferrocenes, made the sodio derivative of tetraphenylcyclopentadiene by the action of sodamide in liquid ammonia.

In the present work protracted attempts to prepare tetraphenylcyclopentadienyl magnesium bromide were unsuccessful, and as experiments with cyclopentadienyl magnesium bromide and 2:6-dimethyl-γ-pyrone yielded no promising results it was not considered to be economical in time to pursue this approach further.

The sodio derivative of tetraphenylcyclopentadiene was therefore prepared and reacted with the γ-pyrone. A light brown product was obtained, which was crystallised from alcohol. Analysis did not correspond to the expected product and dehydration was unsuccessful.

Becker and his co-workers (66) prepared tetraphenylfulvalene by the treatment of tetraphenylcyclopentadienone with cyclopentadienyl magnesium bromide. As a means of testing for the presence of the required organo-metallic

derivative of tetraphenylcyclopentadiene, the suspected material was reacted with tetraphenylcyclopentadienone. No reaction was found with the magnesium derivative; the sodio derivative gave a substance which did not analyse for the expected product, nor did it dehydrate under the conditions used by Becker.

III,9. Chemical Properties of Pyridinium cyclopentadienylides.

Stability.

The stability of the cyclopentadienylides which have been prepared varies greatly with phenylation of the five-membered ring. Thus pyridinium (and picolinium) cyclopentadienylides in the solid state darken slowly on exposure to air, particularly in light, and yet are reasonably stable in solution. This may be illustrated from the effect of exposure on a system in which the ylide, having been freshly precipitated in an aqueous medium, is extracted to some extent into an immiscible organic solvent. The red colour of the solution is retained after considerable darkening of the suspended solid has set in. On the other hand, tetraphenylcyclopentadienylides appear completely stable in the solid state and yet fade in colour rapidly in solution, a benzene solution losing its blue colour after a few hours. In each case stability was enhanced by storing in vacuo, or under nitrogen. Thus a sample of pyridinium cyclopentadienylide sealed off under nitrogen remained without any apparent change for well over a year, and a benzene solution of the tetraphenylated derivative pumped down to a high vacuum, whilst cooled in liquid air, and then sealed off, retained its colour for several months, eventually fading to green and then pale yellow.

The products of decomposition have not been investigated, but in the case of the unphenylated compound

polymerisation almost certainly occurs. The black residue from atmospheric decomposition of a suspension of the ylide in the alkaline medium in which it was formed proved to be completely insoluble in organic solvents and even in boiling aqua regia. The ylide can however be boiled in alkali for a short time without apparent decomposition, although heating in air and in vacuo causes rapid decomposition. An accurate melting point was thus impossible to determine, although introduction of a sample into a previously heated melting point apparatus suggested that it melts at about 200°C but at the same time decomposes rapidly. The tetraphenyl derivative can be melted quite sharply at 210°-211°C to give a red melt.

REACTIONS.

(a) Pyridinium cyclopentadienylide.

Preparation of derivatives.

The ylide failed to form any derivative with either methyl iodide or trinitrobenzene, but formed a yellow-brown picrate. This last was unstable to heat and decomposed to dark coloured tars even in hot reaction mixtures. A derivative was formed from cold solutions, but could not be recrystallised as this caused decomposition. It melted with decomposition at about 95°C.

Complex formation.

On treatment of a benzene solution of the ylide with a solution of benzoquinone in benzene, a deep purple coloration was observed which faded after 20-30 secs., with formation of a dark coloured precipitate. A sample of this was washed well and sent for analysis. It proved to contain very little nitrogen and the result differed little from the figures required for benzoquinone.

An almost exactly similar reaction occurred with chloranil, the initial dark purple colour fading to green. After separation of the dark coloured solid precipitate, the filtrate was evaporated and a green solid of indefinite melting point was obtained. Analysis of this material corresponded fairly well with the figures for chloranil itself.

It seems likely that complex formation does in fact occur, but that the products are quite unstable.

Maleic anhydride addition.

The ylide was allowed to react with maleic anhydride in benzene under an atmosphere of nitrogen. The deep red colour was discharged gradually and the reaction mixture was allowed to stand overnight. A brown precipitate which had settled out from the pale brown liquor was collected. Its insolubility in normal organic solvents prevented recrystallisation and it decomposed before melting. An analysis sample was prepared by thorough washing, but the

results corresponded to no simple adduct, rather indicating that some sort of salt had been formed. This was to some extent supported in that the derivative could be dissolved in sodium hydroxide solution to give a red-brown solution, which on shaking with chloroform gave a slight red coloration to the organic layer, familiar as that from the original ylide.

Substitution reactions.

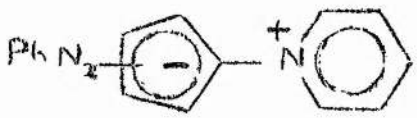
A molecule containing a negatively charged ring would be expected to undergo nucleophilic substitution readily and this has been demonstrated, as mentioned in Section II.1 and II.3 (b), in the case of azulene and ferrocene.

Three typical substitution reactions, bromination, coupling with diazonium salt and Friedel Crafts acetylation, were applied to pyridinium cyclopentadienylide. All gave evidence of some reaction in the manner anticipated.

The bromination was carried out in chloroform solution in an atmosphere of nitrogen. The red colour of the ylide was gradually discharged and a dark coloured deposit obtained which on separation was a dark brown solid, soluble to any extent only in hydroxylic solvents. It decomposed before melting. Analysis gave inconclusive results, but approximated to a substance which might have been formed by substitution of one bromine atom.

On addition of a solution of benzene diazonium chloride to a suspension of the ylide in aqueous methanol, the red

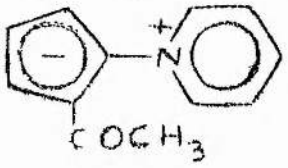
colour deepened. Basification with sodium hydroxide precipitated a very dark coloured solid, which after filtration, decomposed before melting. Recrystallisation was attempted from a variety of solvents without success, the solutions being deep red, and an analysis sample was prepared by the evaporation of a filtered benzene solution. The expected compound might be formulated as XVIII, i.e. $C_{16}H_{13}N_3$. Analysis showed a significant increase in nitrogen content, but the figures corresponded only approximately to $C_{16}H_{13}N_3$.



XVIII

Acetylation was attempted with acetyl bromide, without a catalyst, in dry benzene (cf19). The characteristic ylide colour was rapidly discharged and a brown precipitate was deposited. This appeared granular, but on filtration gave a viscous gum, which however flowed on standing for some time. This effect was thought possibly to be the result of the hydroscopic nature of the material, and after standing in vacuo over concentrated sulphuric acid, a semicrystalline 'skin', which had a distinct odour, was found. This material did not yield either a dinitrophenylhydrazone or an oxime. Formation of these derivatives involved co-ordination by the lone pair from

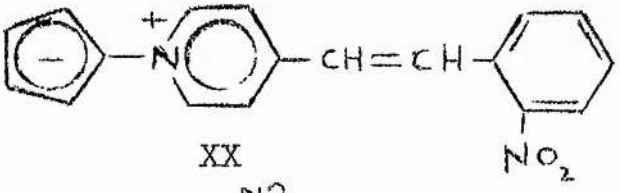
nitrogen with a positive carbon atom. In a structure such as XIX electrons from the five-membered ring would tend to neutralize a positive charge on the carbonyl carbon atom. Thus carbonyl activity might be expected to be reduced.



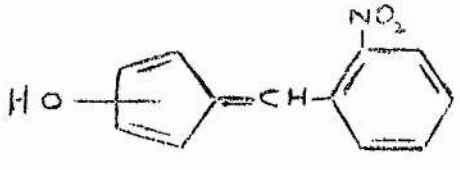
XIX

Reaction with positive carbon atoms.

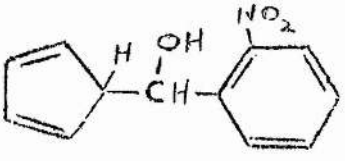
By analogy with the condensation of picolinium salts with aldehydes and ketones (67), γ-picolinium cyclopentadienylide was allowed to stand with nitrobenzaldehyde in an alcoholic solution containing a few drops of piperidine. A solid product almost black in colour was formed, and recrystallised by dilution of a pyridine solution with water. The expected product was XX, but analysis of the dark coloured material correspond rather to a product with the formula $C_{12}H_9NO_3$, or $C_{12}H_{11}NO_3$. Tentative structures for such a compound are the fulvene types XXIa and XXIb.



XX



XXIa $C_{12}H_9NO_3$

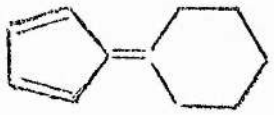


XXIb $C_{12}H_{11}NO_3$

A mechanism for such a reaction would involve a negative carbon from the five-membered ring attaching itself to the positive carbonyl carbon, with simultaneous fission of the carbon-nitrogen bond.

A similar reaction was set up using the unsubstituted pyridinium cyclopentadienylide, and only starting materials could be detected in the product. A repeat experiment using the γ-picolinium ylide also failed to reproduce the earlier result.

Cyclohexanone was reacted under similar conditions with pyridinium cyclopentadienylide, a possible product being the known pentamethylene fulvene (XXII) (70). Only starting materials were recovered.



XXII

(b) Pyridinium tetraphenylcyclopentadienylides.

Preparation of Derivatives.

As in the case of the unsubstituted ylides, no reaction was observed with either trinitrobenzene or methyl iodide, but a yellow crystalline picrate was obtained from alcoholic or benzene solution of either the ylide or its hydrobromide. The picrates crystallised with one molecule of alcohol or acetone, and samples from the two sources were identical. Analysis gave satisfactory results.

Complex formation.

Benzene solutions of the tetraphenylcyclopentadienylide were treated with solutions of benzoquinone and chloranil in benzene. In neither case did the shade of the ylide solution alter, nor was there a precipitate of any insoluble complex.

Maleic anhydride addition.

On shaking a benzene solution of the tetraphenylcyclopentadienylide with maleic anhydride, the blue colour gradually changed to red. A sticky yellow solid which could be recrystallised from ethanol was deposited on the walls of the flask. Analysis did not correspond to any simple addition compound. It is in any case difficult to imagine what structure an adduct would have, as if the normal 1:4 addition took place on an ylide molecule in which the double bonds were thoughtof as fixed, a formal negative charge would have to be accommodated on the 1-carbon atom.

III.10. Physical properties of Pyridinium cyclopentadienylides.

Colour of solutions.

A notable property of the ylides is the range of different colours of their solutions in solvents of varying polarity. The colours are intense and for the unphenylated compound vary from colourless in acidic aqueous solution, through yellow in alkali, orange in alcohols, red in acetone and chloroform, to a reddish-purple in benzene and ether. (See photographs Nos.1a,1b).The phenylated ylide shows a corresponding variation, the solution in alcohol having a red colour, that in chloroform a reddish purple colour and in benzene a deep blue colour. (See photographs Nos. 2a,2b.) Substitution in the pyridine ring does not alter the colour of the ylide sufficiently for it to be detected by the eye.

Kosower (85) has pointed out that these variations in colour are exactly what would be expected if the ylides were "internal" charge transfer complexes.

Spectra.

Reliable Ultra Violet spectra proved impossible to obtain using the Unicam instrument available, as atmospheric interaction caused decomposition. Dr. H.T. Openshaw, of The Wellcome Research Foundation, has kindly consented to arrange for the investigation of these spectra,

as he has additional facilities in particular having a recording instrument.

The results of one determination made on the Unicam instrument, may be noted with the reservation that the figures could not be checked as the material had decomposed by the time the end of the range had been reached. A solution of the pyridinium cyclopentadienylide in chloroform was used. There were peaks at 250 mμ ($\log_{10}\epsilon$ 3.6) and at 520-540 mμ ($\log_{10}\epsilon$ 4.0); the value of $\log_{10}\epsilon$ fell below 3 only between 270 and 320 mμ.

Dipole Moments. (92)

Dr. L.E.Sutton and H.Hely-Hutchinson, of the University of Oxford, have undertaken the measurement of the Dipole Moments of some of the cyclopentadienylides. The results received from them so far are:-

Pyridinium tetraphenylcyclopentadienylide 7.3 ± 0.1D.

γ-picolinium tetraphenylcyclopentadienylide 7.5 ± 0.1D.

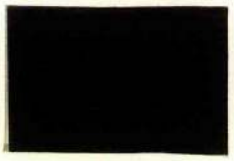
As the methyl group should induce a small dipole moment in the same direction as the ylide, the difference in these two values confirms the direction of the dipole moment in the ylide.

These values agree well with what might be expected, and their magnitudes may be compared with those of :-

6.2D for Dimethyl sulphonium fluorenylide (p.37),

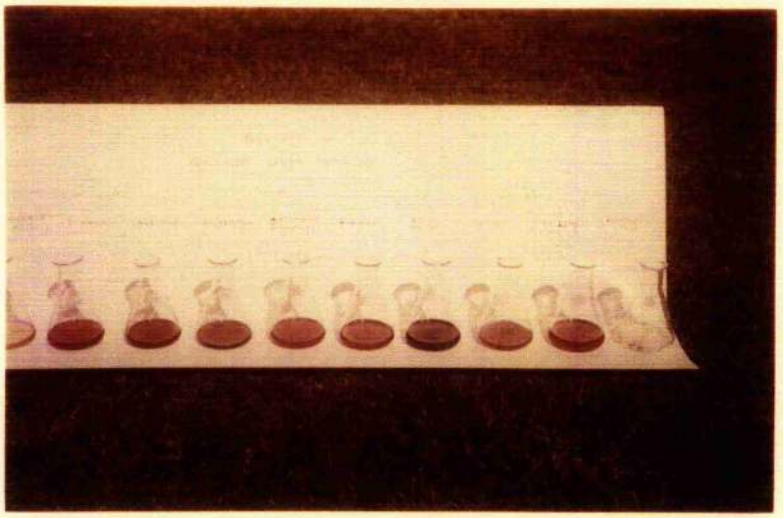
o.99D for Triphenylphosphonium cyclopentadienylide (p.44), and 9.7D for the compound prepared by Kursanov and his co-workers. (XXV p.45).

I a



II a

II b



I b

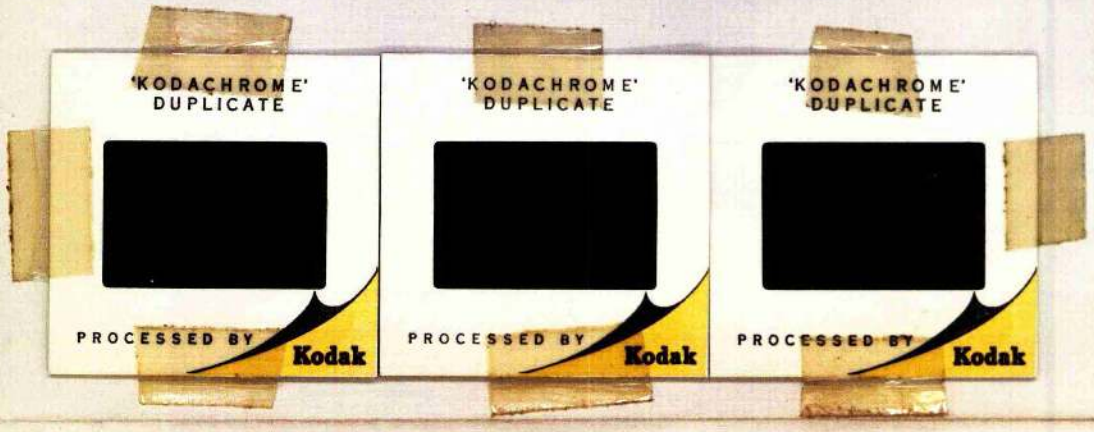
KEY TO PHOTOGRAPHS.

Pyridinium cyclopentadienylide :-

Solid	1a
Solution in various solvents	1b

Pyridinium tetraphenylcyclopentadienylide:-

Solid	2a
Solution in various solvents	2b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IV. Experimental Section.

Preparation of cyclopentadiene.

Dicyclopentadiene was depolymerised to cyclopentadiene by distillation through platinum gauze. This was carried out in an adapted Claisen flask having two bulbs on the vertical outlet arm, each about 5 cms. in diameter, and with a disc of platinum gauze sealed in at the horizontal diameter.

A thermometer (A) was arranged to dip into the dimer, and a second (B) in the vapour of the distilling liquid. The reading of (A) was kept between 160-170°C, and the cyclopentadiene distilled between 40°C and 43°C. The cyclopentadiene was collected in a flask, cooled in an ice/salt bath at -15°C.

Preparation of Dibromocyclopentene, (52)

10 g. of cyclopentadiene and 33 ccs. of chloroform were placed in a flask equipped with a stirrer, a dropping funnel and a calcium chloride tube. The flask was cooled in an ice/salt bath. A solution of 7.5 ccs. of bromine (representing slightly less than one molar equivalent) in 30 ccs. of chloroform was run in slowly, with stirring, over about an hour. The last traces of bromine were washed in with a few ccs. of chloroform.

At the end of the addition the solution was light yellow in colour, but on standing exposed to the air for a few minutes it became a dark blue-green.

This preparation was repeated several times to provide material for the various attempts at ylide formation. In most cases the dibromocyclopentene was used in solution, but in the reactions with ammonia and aniline the chloroform was first removed from a warm water bath, under reduced pressure. Dibromocyclopentene solution 'A' was prepared from 18.1 g. of cyclopentadiene, by the above method. The total volume of the solution was 148 ccs. It was kept, stoppered, in the refrigerator, and the requisite volumes withdrawn when required. Dibromocyclopentene solution 'B' was prepared from 12.5 g. of cyclopentadiene, the total volume of the solution being 114 ccs.

Preparation of Pyridinium cyclopentadienylide.

Because of the comparative instability of the ylide, in most cases it was only prepared from the intermediate immediately before being required. Thus in general, overall yields were not recorded. The difficulty of isolating the intermediate in a suitably crystalline form made it impossible to determine the yield at this stage either.

A specimen preparation was as follows:-

7.7 ccs. of dibromocyclopentene solution 'B' were allowed to stand with 2 ccs. of pyridine for two days. The chloroform was then removed under reduced pressure, at room temperature. Yield of involatile material 5.69 g.

The dark oily residue after removal of the chloroform gradually deposited crystals which appeared to be almost colourless. This involatile residue was extracted with water, filtered, and dilute sodium hydroxide solution added to the filtrate. The red brown crystalline precipitate was collected by filtration, washed with cold water and dried in a vacuum desiccator over phosphorus pentoxide for two hours. Yield 1.58 g. (86.5%)

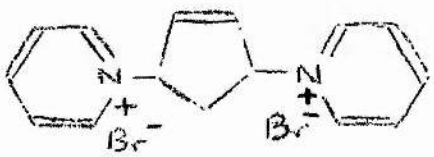
The ylide decomposed to a black insoluble solid on heating alone, but a sample introduced into a melting point apparatus at approximately 200°C showed signs of melting before rapid decomposition set in.

The orange alkaline filtrate contained some dissolved ylide, but in view of the small amount concerned, it was not deemed worthwhile to recover it by extraction with an immiscible solvent, particularly as practical difficulties were encountered, such as formation of emulsions, and difficulty in detecting the interface because of the intensely coloured solutions.

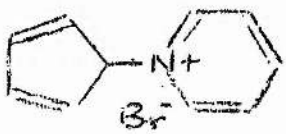
The preparation of the ylide was repeated several times to provide material for various further experiments. The stability of the ylide to the atmosphere was enhanced by allowing the intermediate to stand at room temperature for periods of approximately one year.

Establishment of the nature of the intermediate.

There were two possibilities for the structure of the intermediate, namely dipyridinium cyclopentene dibromide (I) and pyridinium cyclopentadienyl hydrobromide (II).



I



II

The formula I was in fact assigned to the intermediate on the evidence which follows.

The crystalline deposit obtained on removal of chloroform from the intermediate was roughly freed from an adhering dark liquid by rubbing between filter papers, or pressing on a porous plate. Further purification was affected by recrystallisation from alcohol, which however caused some decomposition, and by chromatography.

Alumina was not suitable for this latter purpose as the product decomposed on passing down the column. The initial brown band turned red, presumably by the basic action of the alumina, and faded, probably due to photoxidation.

Hyflo supercel, or filter aid, provided a more satisfactory medium. The material was applied in alcoholic solution, and developed and eluted with an alcohol/ether mixture. Rechromatographing failed to remove the last traces of the brown impurity. M.p. 197°-200.5°C.

Analysis of samples obtained in each of these ways did not correspond with the expected figures. If an average of the analyses were taken, the difference assumed to be oxygen in the form of water, and a correction applied to the average figures, then the results would be found in close agreement with the required values. (Analyses 42, (sample prepared by two recrystallisations from ethanol) 45, 63, (samples purified by chromatography).) A molecular weight determination was not possible as the material was insoluble in compounds such as benzene and camphor.

A picrate was prepared by the addition of a saturated solution of picric acid in ethanol to a solution of the intermediate in hot alohol; it was recrystallised from water, m.p. 195°-196°C. (Analyses 36, 65, 67.) The analysis figures were in each case at some variance with the expected values, carbon being high and nitrogen low.

As formula II involves a cyclopentadiene structure whereas I possesses only one double bond, it was considered that a quantitative study of the addition of bromine to the intermediate should provide information useful in deciding between the two possibilities.

A solution of bromine in ethanol was made up approximately tenth molar. 0.050 g. samples of the intermediate were taken and dissolved in the minimum of methanol. A known excess (10 ccs.) of the bromine solution was added, and the mixture allowed to stand for ten minutes, during which time an orange-yellow precipitate settled out. This was filtered off, dried in vacuo and weighed.

An excess of potassium iodide was added to the filtrate, which was then back titrated with 0.1N sodium thiosulphate solution. The end point was detected conductometrically. A 10 cc. sample of the bromine solution was also titrated in this way, and the amount of bromine used up thereby calculated.

The increase of weight corresponding to the addition of one or two molecules of bromine differs considerably.

Thus for one double bond the uptake by 0.05 g. would be 0.0208 g., and for two double bonds 0.0714 g.

The actual results obtained were:-

10 ccs. of bromine solution reacted with 8.95 ccs. of 0.1N sodium thiosulphate solution.

(1) Weight of product 0.0641 g.

i.e. uptake of bromine 0.0141 g.

Back titration of filtrate required 6.15 ccs. 0.1N sodium thiosulphate solution. Thus bromine equivalent to 2.80 ccs. of 0.1N thiosulphate had been used, that is 0.0224 g.

(2) Weight of product 0.0670 g.

and uptake of bromine 0.017 g.

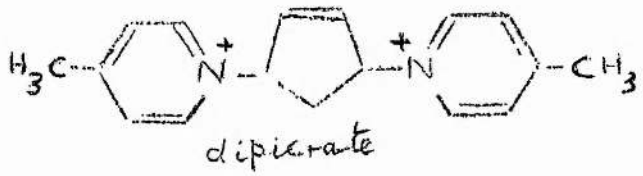
Back titration 6.35 ccs. Bromine used is therefore equivalent to 2.6 ccs. 0.1N thiosulphate, that is 0.0208 g.

These results give definite support to the dipyridinium salt structure for the intermediate.

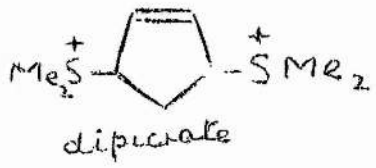
The yellow crystalline bromination product was re-crystallised from ethanol. M.p. 113.5°-115.5°C. (Analyses 43, and 46, both show a high value for bromine, possibly because of absorbed bromine).

The structure I was confirmed by analogy with the results of similar experiments carried out with

γ-picoline and dimethyl sulphide. Although the intermediates themselves were not isolated in these cases, the picrates obtained therefrom analysed correctly for III and IV respectively.



III



IV

Reaction of dibromocyclopentene with one molar equivalent of pyridine.

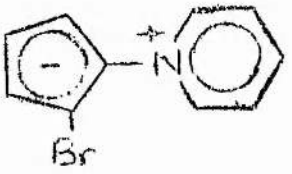
It was hoped that this reaction might provide further information as to the nature of the intermediate in the formation of pyridinium cyclopentadienylide. Confirmation of the dipyridinium structure (II) would have been given if the ylide had been obtained in approximately half the normal yield. In fact a different product was obtained.

1 cc. of pyridine was allowed to stand with 6.7 ccs. of dibromocyclopentene solution "B" for two days. The chloroform was removed under reduced pressure, and the residue, which was not crystalline, was extracted with water. The extract was filtered, using filter cel, and then made alkaline with sodium hydroxide solution. A bright red solid was precipitated and filtered off. Yield 2.4 g. (crude, and dried only at the water pump).

The product darkened slowly on exposure to the air, and was insoluble in benzene, acetone and chloroform. It

dissolved to some extent in water to give a dark brown solution, in hydrochloric acid to give a brown solution, and readily in alcohol to give a blood-red solution (contrast the colour of alcoholic solutions of pyridinium cyclopentadienylide). No melting point could be determined as the material decomposed on heating.

Attempts at recrystallisation also caused decomposition, and an analysis sample was prepared by dilution of a filtered methanolic solution with ether. The analysis figures, (54), were not conclusive. The material contained bromine and a possible structure was V.



V

A picrate was formed from alcohol, but it also decomposed on heating. An analysis sample was prepared from filtered solutions of the material and picric acid. Analysis, (61), did not agree with the figures required for the picrate of V.

It may be noted that if the product were assumed to be a mixture of V and pyridinium cyclopentadienylide, and the proportion of V determined from the bromine figure, then by correcting the analysis figures (54) and (61) appropriately there remain values which correspond well

with those required for pyridinium cyclopentadienylide and its picrate respectively.

Catalytic Hydrogenation of pyridinium cyclopentadienylide.

Absolute alcohol was purified by refluxing with Raney nickel and then distilling.

Adams' platinum oxide catalyst was prepared from platinum chloride by fusion with Analar sodium nitrate.

0.5 g. of pyridinium cyclopentadienylide was dissolved in purified absolute alcohol, and hydrogenated using approximately 0.1 g. of Adams' platinum oxide catalyst. Hydrogen was absorbed steadily for about forty minutes (during which time 330 ccs. of hydrogen had been absorbed) and then more slowly for a further forty minutes, at the end of which time 400 ccs. of hydrogen had been taken up. The absorption tailed off slowly and the experiment was stopped after six hours.

Total uptake of hydrogen (including that absorbed by the catalyst) was 500 ccs. Calculated uptake, for five double bonds, is about 420 ccs.

The catalyst was filtered off and the alcohol from the filtrate removed at the water pump from a warm water bath.

The residue was extracted with a little ether, the extract concentrated and an alcoholic solution of picric acid added. A yellow precipitate was obtained, m.p. 145°-147°C. The melting point of this material was not

depressed on admixture with the picrate from an authentic sample of N-cyclopentylpiperidine.

A second hydrogenation was set up using 5.45 g. of the ylide. Hydrogen was absorbed steadily for four hours (uptake 2,000 ccs.), but thereafter absorption was very slow, even though more catalyst was added. When the experiment was stopped after about 40 hours, the colour of the solution was still quite a deep red.

Total uptake (including catalyst) 3400 ccs.

(Calculated uptake 4,600 ccs.)

The catalyst was filtered off, the alcohol removed and the residue distilled under reduced pressure. 1.5 g. of a pale yellow oil, b.p. 75°-83°C/10-12 mm., were collected.

A picrate was prepared from the product, and recrystallised from alcohol, m.p. 168°C.

Analysis (4), corresponded well for N-cyclopentylpiperidine picrate. A mixed melting point determination with this picrate and an authentic sample of N-cyclopentylpiperidine picrate showed no depression.

An oxalate was prepared in the same way as the oxalate from N-cyclopentylpiperidine, m.p. 170°-171°C. Mixed m.p. with an authentic sample, 170°-174°C.

Preparation of N-cyclopentylpiperidine (53).

Cyclopentanol (71).

10 g. of cyclopentanone were added dropwise to a stirred suspension of 1.4 g. of lithium aluminium hydride in 55 ccs. of dry ether, at a rate which caused gentle refluxing of the ether. At the end of the addition the mixture was refluxed for one hour. The solids were dissolved by running in to the stirred mixture about 130 ccs. of 10% sulphuric acid solution. The ether layer was separated, and the aqueous layer extracted with a further quantity of ether. The combined ether layers were dried over anhydrous sodium sulphate, the ether removed, and the residue distilled through a short column, the fraction b.p. 137°-138°C being collected. Yield 7 g. (70%).

Cyclopentyl bromide, (72).

7 g. of cyclopentanol were placed in a flask fitted with a stirrer, a dropping funnel and a calcium chloride tube. The flask was cooled to 0°C in an ice/salt bath, and 2.75 ccs. (7.8 g.) of phosphorus tribromide added, with stirring, over about an hour, the temperature being kept below 0°C. The stirring was continued for a further two hours and the mixture allowed to stand over the weekend. Water was then added, and the mixture steam-distilled. The lower layer of the distillate was separated, washed with 10% sodium carbonate solution and dried over calcium

chloride. A final distillation was dispensed with. Yield 2.2 g. (18.2%).

This preparation was later repeated on a larger scale, to provide material for the preparation of N-cyclopentylaniline.

N-cyclopentylpiperidine. (53)

2.2 g. of cyclopentyl bromide were heated to boiling, under reflux, with 2.52 g. of piperidine. The contents of the flask soon set to a crystalline slurry. This was taken up in ether, the ether removed and the oily residue distilled under reduced pressure. The fraction b.p. 80°C/10 mm. was collected. Yield 1.1 g. (48%).

Picrate. The condenser from this distillation was washed through with ether, and the washings concentrated down and then treated with picric acid solution. A yellow crystalline picrate, melting point 167°-168°C was obtained.

Oxalate. A few drops of N-cyclopentylpiperidine were heated with a little oxalic acid, and just sufficient water was added to obtain complete solution. On cooling and scratching no crystallisation was effected. A little more oxalic acid was added and the heating and cooling repeated twice, when a crystalline oxalate was formed, m.p. 176°-181°C.

Preparation of cyclic organic bases.

Preparation of 4:5 diphenyl glyoxaline. (55).

(1) 10.5 g. of benzil, 1.3 g. of hexamethylene tetramine, 30 g. of ammonium acetate and 250 ccs. of glacial acetic acid were refluxed together for one hour. The solution was then poured into a large excess of cold water. A slight cloudiness appeared, but no appreciable solid deposit was obtained even on standing overnight.

The bulk of the solution was considerably reduced by evaporation, and on cooling a solid product was obtained. The yield of crude dry material was 10 g. (90%), and after one recrystallisation from ethanol, 5.4 g. of light brown crystals were obtained, m.p. 232°-237°C. Dilution of the liquors with water gave a further 3.3 g. of a buff powder, m.p. 229°-236°C. Total yield 8.7 g. (80%).

(2) 52.5 g. of benzil, 6.5 g. of hexamethylene tetramine, 150 g. of ammonium acetate and 1250 ccs. of acetic acid were heated together under reflux for one hour. After the solution had cooled it was poured into approximately ten litres of water. The resultant turbidity was removed by allowing the mixture to stand with a little norit for a short period, agitating from time to time. The charcoal was filtered off and the glyoxaline precipitated by addition of about one litre of 0.880 ammonia solution. The crude product was crystallised by adding 250 ccs. of hot water to a solution of the product in 250 ccs. of hot pyridine.

The glyoxaline appeared as white glistening crystals, weight 40.2 g., m.p. 232°-230°C. Dilution of the liquors with water gave a further 3 g. of a light brown powder, m.p. 222°-227°C. Total yield 43.2 g. (79%).

Preparation of tetramethylpyrazine, (56).

20 g. of diacetyl monoxime were added gradually to a stirred mixture of 82 g. of stannous chloride and 120 ccs. of concentrated hydrochloric acid contained in a beaker cooled b· ice and salt so that the temperature of the mixture was kept between 5°C and 10°C. At the end of the addition the mixture was diluted with 180 ccs. of water, and then 360 ccs. of 33% sodium hydroxide solution were added gradually, with stirring, the temperature being kept between 40°C and 50°C. A solution of 54.4 g. of mercuric chloride in 120 ccs. of hot water was added, and the mixture was allowed to stand overnight.

The mixture was then steam distilled, and tetramethyl-pyrazine hydrate crystallised from the distillate on cooling. Yield 11 g. (72%).

The free base was prepared by distilling 10 g. of this hydrate. After removal of the water, the base distilled at 188°-190°C. Yield 3.5 g. (40%).

Preparation of 2:3-dimethylquinoxaline, (57).

Diacetyl, (73).

10 g. of diacetyl monoxime and a solution of 32 g. of sodium bisulphite in 70 ccs. of water were allowed to stand overnight at room temperature. The mixture was filtered and 100 ccs. of dilute sulphuric acid were added to the filtrate, which was then distilled from a sand bath until all the yellow oily liquid had come over. This liquid was neutralised with calcium carbonate and distilled again. The distillate was treated with salt and distilled yet again. The yellow upper layer was separated and dried over calcium chloride. The product being in small amount a final distillation was omitted. Yield 0.72 g. (8%).

Condensation of diacetyl with o-phenylene diamine.

A buffer solution of pH 5 was made up from 10 ccs. of 2N acetic acid solution and 100 ccs. of N sodium acetate solution.

0.72 g. of diacetyl and 1 g. of o-phenylene diamine in 55 ccs. of this buffer solution, were allowed to stand together at room temperature. Crystallisation began at once, and after two to three days the light brown product was filtered off. Yield 1.1 g. (83%), m.p. 105°-106°C.

Condensation of diacetyl monoxime with o-phenylene diamine.

1 g. of diacetyl monoxime and 1 g. of o-phenylene diamine were allowed to react, under the same conditions in 55 ccs. of the buffer solution. Brown needle shaped

crystals of the diacetyl monoxime derivative of 2:3-dimethylquinoxaline were formed. Yield 1.45 g. (62.3%), m.p. 180°C.

2:3-dimethylquinoxaline was obtained from this material by treatment with dilute caustic soda solution and extraction with ether.

Preparation of iso-nicotinic acid. (74).

92 g. of γ-picoline and 1500 ccs. of water were heated to boiling under reflux. 380 g. of potassium permanganate were added to the boiling solution in portions of 20-50 g. over about one hour. The permanganate which remained adhering to the sidearm was washed in with water, and at the end of the addition the whole was boiled for a further fifteen minutes. Although no stirrer was employed, awkward bumping was not encountered.

The mixture was filtered hot, and the manganese dioxide retained on the filter was washed with hot water (in two portions the first of 400 ccs. the second 200 ccs.). The combined filtrates were concentrated, under reduced pressure, by heating on a boiling water bath until the volume had been reduced to about 500 ccs. Then the solution was acidified carefully with 100 ccs. of glacial acetic acid, and cooled. The product was filtered off and washed with cold water. A small second crop was obtained by adding a further 50 ccs. of glacial acetic acid to the filtrate.

The white crystalline solid held tenaciously to water, and was dried by washing with a little alcohol, drying in a desiccator over anhydrous potassium carbonate and sodium hydroxide and then in the oven. Yield 80 g. (66%), m.p. 285°-290°C.

One recrystallisation from hot water raised the melting point of a sample to 312°-316°C, and any material to be used was first purified in this way.

Reaction of dibromocyclopentene with various organic bases.

The reactions were carried out in almost exactly the same manner in each case. 1 g. of the base was taken, a little chloroform added and the calculated volume of a chloroform solution of dibromocyclopentene added. The mixture was allowed to stand for one or two days, and the chloroform then removed under reduced pressure at room temperature.

α-picoline.

2.9 ccs. of dibromocyclopentene solution 'A' were used. A sample of the residue, after removal of the chloroform, was extracted with water, and the extract made alkaline with dilute sodium hydroxide solution. A red-brown cloudiness appeared, but no precipitate was obtained. On shaking with chloroform the organic layer was coloured deep red, in the same way as with the pyridinium ylide.

The rest of the residue was left at room temperature for about one and a half years, and then tested with dilute

sodium hydroxide solution. A crystalline red-brown precipitate was formed slowly, much more rapidly if a 40% sodium hydroxide solution was used.

No further work was done on the ylide prepared in this way.

β-picoline.

The product from β-picoline was treated in exactly the same way. In the first basification a very dark red amorphous precipitate was formed, which imparted the familiar coloration to chloroform.

The alkaline treatment of the product after the prolonged standing yielded a red-brown crystalline precipitate as with pyridine.

γ-picoline.

On treatment with alkali a red-brown crystalline precipitate was obtained, which compared almost exactly with pyridinium cyclopentadienylide. The product was slightly browner in colour and was a little more stable to the atmosphere.

In an experiment using 5 ccs. of γ-picoline and 14.5 ccs. of the dibromocyclopentene solution 1.85 g. (44%) of γ-picolinium cyclopentadienylide were obtained.

On treatment of the intermediate with alcoholic picric acid solution, a picrate was formed which was recrystallised from boiling water, m.p. 223°-225°C. Analysis (66) agreed well with the required value for

di-γ-picolinium cyclopentene dipricate.

Attempted hydrogenation of γ-picolinium cyclopentadienylide.

A hydrogenation was set up as with the pyridinium ylide but using 0,88 g. of γ-picolinium cyclopentadienylide. A negligible volume of hydrogen was absorbed even after several hours shaking, and addition of a further quantity of the catalyst.

A fresh batch of Adams' catalyst was prepared, a more careful control of the temperature of fusion being exercised by use of a thermocouple. The activity of this catalyst was tested by hydrogenating cyclohexene, the calculated volume of hydrogen being absorbed briskly.

A second hydrogenation of the ylide was attempted using this fresh catalyst but again only a very small volume of hydrogen was absorbed. In neither case was the red colour of the solution discharged, and the ylide could be recovered by removal of the solvent.

2:6-lutidine.

2.5 ccs. of dibromocyclopentene solution 'A' were used. Initially very little coloured material was formed on addition of alkali to the aqueous extract of the residue after removal of chloroform.

After the mixture had been allowed to stand at the intermediate stage for one and a half years, alkaline treatment produced some crystalline precipitate of red-brown 2:6-lutidinium cyclopentadienylide, which gave the

usual colour in chloroform.

2:4:6-collidine.

2.2 ccs. of dibromocyclopentene solution 'A' were used. On initial addition of the sodium hydroxide solution no coloured products were obtained. The product which had been allowed to stand for one and a half years yielded a small amount of a dark red precipitate on treatment with 40% sodium hydroxide solution, and the familiar red coloration was obtained on shaking a small quantity of the alkaline mixture with an organic solvent.

An alcoholic solution of the intermediate, which had crystallised after the prolonged standing, was treated with saturated ethanolic picric acid. A brown precipitate was formed, which was collected by filtration. This proved to be an intractable gum which could not be crystallised from water, or any of the common organic solvents. The alcoholic filtrate, after separation of this precipitate, was allowed to stand for two to three days when a brown deposit was obtained. After crushing and recrystallising from water, a bright yellow crystalline product was obtained, m.p. 152°C. A mixed melting point determination confirmed this to be the picrate of 2:4:6-collidine (m.p. 156°C).

isoQuinoline.

2.1 ccs. of dibromocyclopentene solution 'A' were used. No coloured materials were formed when the reaction product was treated with sodium hydroxide solution, concentrated or dilute, hot or cold, even after the residue had been allowed to stand for sixteen months.

A picrate prepared from an alcoholic solution of the intermediate, and recrystallised from water, proved to be almost entirely isoquinolinium picrate, although some slight decomposition was observed just below the melting point. (Analysis, 70).

Quinoline.

2.1 ccs. of dibromocyclopentene solution 'A' were used. The product from the reaction was treated as in the isoquinoline experiment but no evidence of ylide formation was obtained. On addition of alkali a cloudiness was formed, presumably an emulsion of precipitated quinoline.

Tetramethylpyrazine.

2 ccs. of dibromocyclopentene solution 'A' were used. The product from the reaction was treated as in the quinoline experiment with similar failure to produce any ylide.

2:3-dimethylquinoxaline.

1.7 ccs. of dibromocyclopentene solution 'A' were used. Alkaline treatment of the residue after removal of

chloroform yielded no coloured material.

A picrate was formed from an alcoholic solution of the intermediate. This picrate was recrystallised from alcohol. Large dark green fern-like crystals were formed, m.p. 196°-197° C. The picrate was shown, by mixed melting point with an authentic sample, to be the picrate of 2:3-dimethyl quinoxaline.

4:5-diphenylglyoxaline.

Dibromocyclopentone was prepared, in chloroform, from 3 g. of cyclopentadiene and 2.15 ccs. of bromine. This solution was added with stirring to a suspension of 20 g. of 4:5-diphenylglyoxaline in approximately 300 ccs. of chloroform. Stirring was continued for about 17 hours during which time no reaction was observed. The mixture was then refluxed on the water bath for 5-6 hours, and the solvent removed. A buff precipitate of unreacted glyoxaline remained.

The temperature of reflux was raised by dissolving in alcohol, but after several days refluxing, no reaction had taken place, and no coloured materials were obtained on treatment of a sample with sodium hydroxide solution.

Trimethylamine and Triethylamine.

4.5 ccs. of dibromocyclopentene solution 'A' were mixed respectively with 2.5 ccs. of triethylamine and 3 ccs. of trimethylamine solution in alcohol (33% w/w), and allowed to stand. The chloroform was removed, but

the residue in neither case gave a coloured product on treatment with dilute sodium hydroxide solution.

In view of Spooncer's preparation of trimethylammonium cyclopentadienylide (47), these products were retested rather more than a year later. A very small amount of coloured material was formed by warming the triethylamine intermediate with 40% sodium hydroxide solution. An ammoniacal smell was noticed, and on extracting with chloroform a very pale red-brown organic layer was obtained. No solid coloured material was obtained. The trimethylamine experiment gave no promising results.

A picrate was formed from an alcoholic solution of the intermediate from triethylamine. The picrate was recrystallised from boiling water, and depressed the melting point of a sample of triethylamine picrate. The picrate of the intermediate decomposed over a range 230°-246°C. (Analysis 69.)

5:7-dimethyl-2:3-benzo-1:4-diazepine.

1 g. of the diazepine in a few ccs. of chloroform was allowed to stand with 1.5 ccs. of dibromocyclopentene solution. After a few minutes the deep red of the diazepinium cation was visible. After two or three days the solution was strongly red coloured, and the normal working up procedure was made difficult by the constant presence of this deep coloured material. An attempt to separate the diazepine from any ylide formed, by

differential extraction of an alkaline solution of the reaction product with chloroform, failed as the interface was completely obscured by a dark coloured solid, insoluble in chloroform, adhering to the walls of the separating funnel.

isoNicotinic acid.

4. 1 g. of isonicotinic acid were suspended in about 25 ccs. of chloroform and 10 ccs. of dibromocyclopentene solution 'B' were added. The blue-green colour of the solution was discharged. The mixture was allowed to stand with occasional shaking for several days, during which time the chloroform had evaporated. A sample of the residue was treated with sodium hydroxide solution, but even on heating with a 40% solution no evidence of any coloured product was obtained.

Ammonia.

Dibromocyclopentene was prepared in the usual way from 10 g. of cyclopentadiene, the chloroform being removed under reduced pressure from a warm water bath. The dibromo compound was then added with shaking to 20 ccs. of 0.880 ammonia solution, which was cooled by acetone/ solid carbon dioxide. A dark brown lower layer appeared but no vigorous reaction was observed. The stopper was then wired in, using a piece of rubber tubing as a safety valve, and the shaking continued with an automatic shaker. After about thirty minutes the pressure generated in the

flask was sufficient to blow out the stopper. The shaker was stopped and the mixture allowed to stand overnight.

The reaction mixture was red, with a white crystalline deposit (presumed to be ammonium bromide) and some dark tarry material.

A sample was withdrawn and diluted with water. The solution was red, but the tarry material remained undissolved. The red coloured material could not be extracted into chloroform, ether, ethyl acetate or benzene; extraction with methylene chloride was more successful, although separation of the layers was difficult, and some dark coloured material was formed during the process, and stuck to the walls of the separating funnel. The extract was dried and the solvent removed, under reduced pressure, on a warm water bath. A deep red viscous gum remained, which could not be crystallised. It was insoluble in water, but was soluble in alcohol and methylene dichloride.

An alcoholic solution of this gum gave a yellow precipitate with picric acid solution, the melting point was indistinct but in the range 120°-160°C. Attempts at the preparation of a pure sample were defeated by the rapid decomposition of the picrate on warming in solution.

Attempts at the preparation of a trinitrobenzene adduct or an acetyl derivative failed to yield satisfactory products.

Aniline.

Dibromocyclopentene was prepared from 10 g. of cyclopentadiene as before, and added gradually with mechanical stirring to 30 ccs. of aniline contained in a flask cooled in an ice/salt bath. After about ten minutes the stirrer was slowed considerably by precipitated solid, and when all the dibromo compound had been added the reaction mixture was practically solid.

The reaction mixture was extracted several times with chloroform, the extracts being filtered to remove the white anilinium bromide. The chloroform extract was washed with water and dried over calcium chloride.

The solvent was removed from a portion of the extract. The residue was a dark red viscous liquid, which on removal of the last traces of solvent in a vacuum desiccator, gave a puffy plastic-like material which crumbled to a light red-brown solid, m.p. *ca.* 90°C. Recrystallisation was very difficult as tarring took place on warming, even in a low boiling solvent such as methanol. An analysis sample was prepared by cooling an alcoholic solution in acetone/solid carbon dioxide. Analyses, (1) and (62), did not correspond to any simple ylide structure.

No satisfactory derivatives were obtained. A yellow picrate was formed from an alcoholic solution, but it darkened very rapidly on warming. Acetylation with acetic anhydride was attempted but only starting materials were

obtained. Similarly refluxing with methyl iodide was unproductive.

Catalytic Hydrogenation.

1.65 g. of the crude red-brown material were dissolved in 350 ccs. of ethanol (previously refluxed with Raney nickel and distilled) and 60 ccs. of ethyl acetate. The solution was shaken with Raney nickel, filtered, and hydrogenated at room temperature using a little Adams' platinum oxide catalyst. Hydrogen was absorbed slowly. Total uptake, including hydrogen absorbed by the catalyst, 470 ccs. (theoretical uptake for two double bonds approximately 450 ccs.).

The catalyst was filtered off and the solvents distilled from the water bath. The residue was distilled under reduced pressure, the main fraction, b.p. 140°C/14 mm., being taken.

A concentrated alcoholic solution of this material was treated with picric acid solution, but no derivative was formed even after warming, cooling, scratching and allowing to stand for twenty-four hours.

A little of the distillate was heated with acetic anhydride on the water bath for half an hour. The mixture was poured into cold water, and after scratching and adding ammonia solution a white solid product was obtained, melting point 105°C. A mixed melting point with the acetyl derivative of N-cyclopentylaniline (m.p.89°-91°C) was 60°C.

A mixed melting point with acetanilide (m.p. 112°C) was 106°C, indicating that this was the product. There was, therefore, no real evidence of the formation of the required ylide or its reduction product, (but see III,6).

Preparation of N-cyclopentylaniline, (53).

1 cc. of cyclopentyl bromide was heated with 1.8 ccs. of aniline for a few minutes. The mixture was allowed to cool and was extracted with ether, the ether removed and the residue distilled under reduced pressure, the fraction b.p. 135°C/12 mm. being taken.

Acetyl derivative.

A little N-cyclopentylaniline was heated on the water bath with acetic anhydride for half an hour. The reaction mixture was poured into cold ammonia solution and the white crystalline product (m.p. 89°-91°C) collected by filtration.

Preparation of phenylated cyclopentadienes.

Preparation of 2:3:4:5-tetraphenylcyclopentadiene (54).

(1) Desoxybenzoin, (75).

220 g. of benzoin were dissolved in 380 ccs. of glacial acetic acid in a three necked flask fitted with a mechanical stirrer and a water condenser. The flask was heated in an oil bath; the temperature of the oil was about 160°C, with the contents of the flask at about 95°C at solution.

66.7 g. of zinc were then added as rapidly as possible, care being taken to avoid excessive frothing. The acetic acid was by now refluxing briskly and on settling down the bath temperature was approximately 155°C, with the contents of the flask at 125°C. The refluxing was continued for about eight hours, by which time a sample withdrawn no longer gave a flocculent precipitate when added to cold water.

The mixture was poured into hot water and boiled until the oil collected at the bottom. It was then cooled, filtered and the solid washed with water and dissolved in ethanol. The zinc was removed by filtration and the alcoholic solution distilled under reduced pressure. The alcohol was removed at water pump pressure on the water bath but the desoxybenzoin did not come over at this pressure. It distilled at about 3 mm. pressure when heated in an oil bath, and solidified in the receiving flask.

Yield 162 g. (79.6%).

(2) Methylene bisdesoxybenzoin.

162 g. of desoxybenzoin were suspended in a mixture of 650 ccs. methanol and 30.8 g. of 40% formaldehyde solution. A solution of 46.8 g. of potassium hydroxide in 27.5 ccs. of water and 160 ccs. of methanol was added, and the whole stirred mechanically. The mixture became yellow in colour, and the desoxybenzoin formed a thick, almost solid oil. After 2½-3 hours stirring, the methylene bisdesoxybenzoin had come out as a fine white solid. This was collected by filtration, washed with methanol and dried at the pump, and then in a vacuum desiccator overnight. Yield 130 g. (78.3%), m.p. 145°-146°C. The product was sufficiently pure to continue without further treatment.

(3) 2:3:4:5-tetraphenyl-3:4-dihydroxycyclopentane.

The large volumes of acetic acid involved necessitated the next stage being done batch wise.

The diketone was dissolved in boiling glacial acetic acid, and zinc dust added over three hours. The mixture was boiled for a further hour and the hot solutions were decanted from the zinc into an excess of cold water. The separate portions of zinc were then each extracted twice with 100 ccs. of boiling glacial acetic acid and the extracts were added to the main bulk.

The sticky precipitate which formed was filtered off, and then boiled up with water so that it filtered more

readily.

The quantities used were: Batches (1) and (2) 45 g. methylene bisdesoxybenzoin, 750 ccs. glacial acetic acid, and 135 g. zinc dust. Batch (3) 40 g. methylene desoxybenzoin, 660 ccs. glacial acetic acid and 120 g. zinc dust.

(4) Dehydration to 2:3:4:5-tetraphenylcyclopentadiene.

The damp filter cake of the dihydroxy compound was dissolved in one litre of hot glacial acetic acid, and a solution of 65 ccs. of concentrated sulphuric acid in 145 ccs. of glacial acetic acid was added. The mixture was boiled and after a few minutes the hydrocarbon separated as fine, almost colourless needles. After ten minutes the mixture was allowed to cool, filtered and the product washed with glacial acetic acid followed by a little methanol. Yield 70 g. (60% based on the diketone). m.p. 178°C.

At the end of stage (2) the liquors were allowed to stand overnight, and a yellow crystalline solid was deposited. This was collected by filtration. Weight 12 g., m.p. (crude) 96°C, after two recrystallisations from ethanol, m.p. 94.5°C.

A sample of this material analysed correctly for benzil, (13) and was shown to be benzil by mixed melting point with

an authentic sample. The melting point of the dinitrophenylhydrazone, (185°-189°C), also corresponded with that from benzil (m.p. 189°C).

The liquors, after separation of the benzil, were again set aside and after three or four weeks standing a further 6 g. of a white solid were deposited. Its melting point was 145°-146°C, indicating that it was methylene bisdesoxybenzoin.

Preparation of 2:5-diphenylcyclopentadiene.

(a) β-benzoylpropionic acid. (76).

In a two litre round bottomed flask, fitted with a mechanical stirrer and two reflux condensers, were placed 68 g. (0.68 mole.) of succinic anhydride and 350 g. (4.5 moles.) of sodium dried benzene. The stirrer was started and 200 g. (1.5 moles) of powdered anhydrous aluminium chloride were added all at once. The reaction mixture heated up and hydrogen chloride was evolved. The flask was then heated to reflux in an oil bath for half an hour with efficient stirring.

The mixture was cooled by surrounding the flask in cold water, and 300 ccs. of water were slowly run in through a dropping funnel fitted to the top of one of the condensers. 100 ccs. of concentrated hydrochloric acid were added and the benzene removed by steam distillation.

The hot residue was transferred to a one litre beaker, when the β-benzoylpropionic acid separated as an oil which soon solidified. After cooling to $0^{\circ}C$, it was collected at the water pump and washed successively with a cold mixture of 50 ccs. of concentrated hydrochloric acid and 150 ccs. of water, and 200 ccs. of cold water.

The crude acid was then dissolved in a solution of 75 g. of anhydrous sodium carbonate in 500 ccs. of water by boiling for 15 minutes. The hot solution was filtered,

with suction, and the small amount of aluminium hydroxide retained on the filter was washed twice with 50 cc. portions of hot water.

4 g. of charcoal were added to the combined filtrates and the whole stirred for a few minutes. The charcoal was filtered off, and the clear colourless filtrate transferred to a two litre beaker. The solution was acidified carefully with 130 ccs. of concentrated hydrochloric acid, and after cooling to $0^{\circ}C$ in an ice/salt bath the acid was collected and washed well with cold water.

The product was dried overnight at room temperature in a vacuum desiccator and then dried to constant weight at 40°-$50^{\circ}C$. Yield 96 g. (79%), m.p. 114°-$115^{\circ}C$.

(b) Ethyl β-benzoylpropionate.

The esterification was carried out using various proportions of reactants, and durations of reflux, the working-up procedure being the same in each case.

(1) 20 g. of β-benzoylpropionic acid, 25 ccs. of absolute alcohol and 1 cc. of concentrated sulphuric acid were refluxed together for twelve hours. At the end of the reflux the excess alcohol was distilled off, some water added and the mixture extracted well with ether.

The ether extract was washed with sodium carbonate solution and then with water, and dried over anhydrous sodium sulphate. The ether was removed and the ester distilled under reduced pressure on an oil bath.

The sodium carbonate extract was acidified carefully with hydrochloric acid, and a white precipitate of unreacted acid (1 g.) obtained. The percentage yield of the ester was calculated on the basis of unrecovered acid. Yield of ethyl β-benzoylpropionate 11.14 g. (50.7%), b.p. 124°-128° C/1.5 mm.

Subsequent runs:-

(2) Quantities:- 10 g. β-benzoylpropionic acid, 1 cc. concentrated sulphuric acid, 40 ccs. absolute alcohol. Refluxed for 24 hours. Recovered acid 0.7 g. Yield of ester: 1st fraction 4.5 g., b.p. 126°-130°C/2 mm. Refractionation of 2nd cut 2.3 g., b.p. 126°-130°C/2 mm. Total yield 6.8 g. (63%).

(3) Quantities:- 10 g. acid, 1 cc. concentrated sulphuric acid, 40 ccs. absolute alcohol. Refluxed for 40 hours. Recovered acid - negligible. Yield of ester 2.04 g., b.p. 126°-130°C/2 mm. The flask was broken during the working up, but as the amount of acid recovered was small, a better yield was to be expected and a similar run was set up.

(4) Conditions as (3), but a slightly larger volume of alcohol. Recovered acid - negligible. Yield of ester 9.14 g. (79%), b.p. 124°-130°C/2 mm.

(5) Quantities:- 20 g. acid, 2 ccs. concentrated sulphuric acid, 45 ccs. absolute alcohol. Refluxed for 45 hours. Recovered acid - negligible. Yield of ester 19.82 g. (85.6%), b.p. 120°-126°C/1.5 mm.

(c) 2:5-diphenylcyclopentadiene, (62).

2.45 g. (.103 g. atoms) of clean sodium were dropped, in small pieces, down a water condenser into about 70 ccs. of dry alcohol. The last traces of sodium were dissolved by warming on the water bath, and the excess alcohol was then removed under reduced pressure.

The sodium ethoxide thus obtained was mixed with 100 ccs. of sodium-dried benzene and 11 g. of ethyl β-benzoylpropionate were added. The mixture was shaken occasionally to complete the solution of most of the sodium ethoxide and 6.5 g. of acetophenone were added. The flask was stoppered and allowed to stand at 40°C for 24 hours, during which time the solution became a deep orange-red colour.

The mixture was cooled in an ice bath, poured into 500 ccs. of ice water, transferred to a separating funnel and shaken well. When the separation of the benzene layer was completed the aqueous layer was withdrawn and warmed on the water bath to about 60°C. After several minutes pale coloured crystals of 2:5-diphenylcyclopentadiene appeared, and when these ceased to separate they were

filtered off and washed well with water. After one recrystallisation from alcohol the yield was 1.5 g. (12.8%), m.p. 157°-160°C.

Preparation of 1:3-dibenzoylpropane.

(a) Ethyl benzoylacetate. (77).

600 ccs. of absolute alcohol were placed in a two litre 3-necked flask mounted on a water bath and fitted with a reflux condenser, a dropping funnel and a sealed stirrer. 46 g. (2 g. atoms) of clean sodium were cut into small pieces and added gradually down the condenser. The sodium ethoxide solution was stirred and cooled to room temperature. 267 g. (260 ccs. 2.05 moles.) of ethyl acetoacetate were run in slowly. The stirrer was replaced by an air bleed, guarded by a drying tube, and the condenser by a short still head. The alcohol was then distilled off at about room temperature at the water pump. After about half the alcohol had been removed a considerable amount of the sodium enolate had been precipitated. The residue appeared dry after about two hours, and the last traces of alcohol were removed at 2 mm. pressure on a boiling water bath.

The flask was allowed to cool under reduced pressure, and 600 g. (570 ccs. 4 moles.) of ethyl benzoate added to the residue, the vacuum having been released. The flask was then heated in an oil bath at 140°-150°C for six hours. Over about one hour the temperature of the bath was raised

to 180°C, during which time an ethyl acetate alcohol mixture began to distil. Eventually about 200 ccs. of distillate (mainly ethyl acetate) was collected at this temperature.

The reaction mixture was cooled, 250 ccs. of water were added and the solution made acid to litmus by addition of a cooled solution of concentrated sulphuric acid, and 200 ccs. of water. Chipped ice was added to keep the mixture cool.

The upper ester layer was separated, and the aqueous layer extracted with 200 ccs. of ether. The ether and ester layers were shaken with 350 ccs. of saturated sodium bicarbonate solution, until the evolution of carbon dioxide ceased. The organic layer was washed with 200 ccs. of water, and then the combined water and bicarbonate layers were extracted with 400 ccs. of ether. The combined ether and ester layers were dried over anhydrous sodium sulphate and the ether removed from the water bath.

The excess ethyl benzoate and ethyl aceto-acetate were distilled off under reduced pressure, 350-400 ccs. of distillate being collected at about 80°-90°C/12 mm.; a 15 cm. fractionating column was used. The ethyl benzoyl acetate was distilled through a short Claisen head from the oil bath. Yield 206 g. (53%), b.p. 120°-124°C/1.5-2 mm.

(b) Ethyl dibenzoylglutarate.

Japp and Michie's method (63) was used, with the modification that in all but the first run alcohol was added at the start to give a more homogeneous reaction mixture.

(1) 10 g. of ethyl benzoylacetate and 2 ccs. of 40% aqueous formaldehyde solution were mixed and 1.5 ccs. of piperidine added gradually with cooling and shaking. On thickening a little alcohol was added. A thick cake was obtained, and the material was recrystallised once from alcohol. Yield 7.1 g. (69%), m.p. 87°-88°C (Japp and Michie give the m.p. as 92.5°C).

(2) Same quantities as (1), 15 ccs. of alcohol were added at the beginning and the mixture was stirred in a small beaker cooled in an ice bath. Yield 8.85 g. (85.5%), m.p. 81°C.

(3) As (2) using 50 ccs. alcohol. Yield 8.55 g. (83%). The product was whiter, and melted at 89°C without recrystallisation.

(4) 154 g. of ethyl benzoylacetate, 31 ccs. of 40% formaldehyde solution, 420 ccs. of alcohol and 23 ccs. of piperidine were used. The mixture was stirred for half an hour. Yield 160.2 g. (99%), m.p. 88°-89°C. The product was a good white colour.

(c) 1:3-Dibenzoylpropane. (63).

7 g. of dibenzoyl glutaric ester were boiled, under reflux, with 35 ccs. of a mixture of equal parts of concentrated sulphuric acid and water. During the reflux some orange, resinified material appeared on the surface of the liquid. At the end of the heating the flask was cooled under the tap with vigorous shaking and the product precipitated in coarse granular form. At the same time the solution assumed a green-blue fluorescence, which persisted for several days. The precipitate was collected on a sintered glass funnel and taken up in warm ether. The ethereal solution was shaken with sodium carbonate solution, dried over anhydrous calcium chloride and the ether removed. The dibenzoyl propane appeared as yellow plates. Crude yield 3.7 g.

One recrystallisation from ethanol gave 2.65 g. of an almost white product (60%), m.p. 65°-67°C.

Further runs were carried out using the same method:-

(2) 15.4 g. of dibenzoyl glutaric ester, 77 ccs. of the acid mixture. An oily semi-solid product was obtained, which proved to be the starting material (m.p. 86°-87°C). 5.55 g. only of the ester were recovered.

(3) 5.55 g. of ester, 27 ccs. of the acid mixture. Crude yield 3.5 g. (99%).

(4) 50 g. of ester, 250 ccs. of the acid mixture. Crude yield 30 g.

(5) 75 g. ester, 390 ccs. of the acid mixture. Crude yield 40 g. Yield for (4) and (5) 88%.

The products from (3), (4) and (5) were recrystallised together, from alcohol. The liquors were evaporated down and recrystallised from petroleum ether.

The melting point of the yellowy white product was 65°-67°C.

Attempted ring closure of 1:3-Dibenzoylpropane.

Japp and Michie (63) prepared 1:2-diphenylcyclopentane-1:2-diol by reduction of dibenzoylpropane with aluminium amalgam in wet alcohol. This method, which takes about three weeks, was tried without success. Various other pinacone reduction reactions were tried without success, dibenzoyl propane being recovered in each case. Particular attention was paid to the reduction using zinc in boiling acetic acid, on account of its simplicity and its successful application in related cases, namely reduction of methylene bisdesoxybenzoin to 2:3:4:5-tetraphenyl-3:4-diol (54), and in the preparation of 1:2:4-triphenylcyclopentadiene (69).

(a) Reduction with aluminium amalgam in wet alcohol (63).

1.55 g. of aluminium were degreased by extraction with ether for four hours in a Soxhlet extractor, and were then shaken for a few seconds with 1.6 ccs. of a saturated solution of mercuric chloride in ethanol, and 15.5 ccs. of ethanol. The amalgam was filtered off as rapidly as possible, washed with a little alcohol and added to

1.55 g. of dibenzoylpropane in a mixture of 31 ccs. of ethanol and 15.5 ccs. of water, contained in a round bottomed flask to w.ich a condenser was then attached.

The flask was heated on a water bath through the day, and allowed to stand overnight. This treatment was continued for three or four weeks, a further portion of 1.55 g. of aluminium powder, treated as before, being added after about ten days.

At the end of this period the mixture was filtered, and some of the alcohol in the filtrate was distilled off. The residue was cooled overnight in the refrigerator, when an oily precipitate was obtained, some of which was retained on a filter paper. This proved to be recovered dibenzoyl-propane, as a sample crystallised from alcohol had m.p. 60°C and mixed melting point 58°-62°C with dibenzoyl propane (m.p. 65°-67°C) indicating that the reaction had been unsuccessful.

(b) Reduction with Magnesium Amalgam.

Magnesium amalgam was prepared from 0.6 g. of magnesium and a little mercury by grinding them together in a warm mortar. The amalgam was suspended in dry benzene, and a solution of 1 g. of dibenzoylpropane in dry benzene was added. No signs of a vigorous reaction were observed, and after refluxing on the water bath for two hours the mixture was hydrolysed by further heating with water. The magnesium was filtered off and the

benzene layer in the filtrate separated, dried over anhydrous sodium sulphate and the solvent removed.

The residue, a sticky yellow material, was recrystallised from ethanol, m.p. 57°C. Mixed m.p. 58°-60°C with dibenzoylpropane. This showed it to be unreacted starting material.

(c) Magnesium-Magnesium iodide reduction (78).

0.5 g. of magnesium was suspended in a mixture of dry benzene and ether, and 1 g. of iodine was added through the condenser fitted to the containing flask. The mixture was warmed slightly to start the reaction, and then left for one hour. A solution of 1 g. of dibenzoylpropane in benzene was added, and a yellowish white complex formed which did not dissolve completely on shaking.

This solid was filtered off, and extracted with benzene. The filtrate and benzene extract were combined with water. No precipitate was obtained, and the organic layer became milky. (A pink coloration was discharged with sodium bisulphite). The milkiness was not cleared up by addition of a little dilute hydrochloric acid solution. The organic layer was separated, dried over anhydrous sodium sulphate and the clear yellow solution was evaporated. A light brown crystalline product was obtained, m.p. 63°C. Mixed m.p. with dibenzoylpropane 60°-62°C.

(d) Reduction with zinc and glacial acetic acid.

(1) 1 g. of dibenzoylpropane was dissolved in 25 ccs. of boiling acetic acid, and 5 g. of zinc powder were added portionwise to the refluxing solution, over approximately two and a half hours. The mixture was refluxed for a further two hours, and filtered hot, the filtrate being run into an excess of ice and water. The residual zinc was extracted with a few ccs. of boiling acetic acid and the extract added to the filtrate. After standing overnight the precipitate was filtered off, and a sample rubbed on a porous plate, m.p. 58°-60°C. Mixed melting point with dibenzoylpropane showed no depression.

The reaction was repeated with the recovered material, this time using zinc dust in place of zinc powder. The product was very sticky, but was proved to be unreacted starting material by melting point and mixed melting point determination.

Before further attempts were made the glacial acetic acid to be used was purified by distilling it from potassium permanganate and then redistilling it from acetic anhydride through an eight inch column.

(2) Experiment (1) was repeated using exactly the same quantities, both zinc dust and then zinc powder (20-50 mesh) being employed. In each case a reasonably granular product was obtained, which proved to be dibenzoylpropane.

(3) As experiment (2), but using zinc dust from a different source. Although the refluxing was continued for eight hours in all, only starting material was recovered.

(4) As experiment (2) using 50 ccs. of glacial acetic acid and zinc powder. One crystal of copper sulphate was added to the reactants. The product was very sticky and a solution in acetone was chromatographed on a short alumina column, eluting with ether. Only starting material was identified in the eluates.

Preparation of 1-bromo-2:3:4:5-tetraphenylcyclopentadiene (59).

(a) Using N-bromosuccinimide on tetraphenylcyclopentadiene.

A trial run was carried out on a small scale. 0.86 g. of tetraphenylcyclopentadiene, 0.49 g. of N-bromosuccinimide and 30 ccs. of carbon tetrachloride were refluxed together for one and a half hours. The succinimide was filtered off at the pump and washed with a further quantity of carbon tetrachloride. The filtrate and washings were concentrated under reduced pressure, and the yellow bromo-product which precipitated was filtered off. Yield 0.89 g. (85.7%), m.p. 185°-190°C.

The material was normally used without further purification, but could be recrystallised from a chloroform-methanol mixture.

Subsequently the preparation was repeated using the same proportions of reactants.

(1) Using 10 g. of hydrocarbon. Yield 6 g. (50%).

(2) Using 10 g. of hydrocarbon. First crop 6 g. Second crop (on further concentration of the liquors) 2.4 g. Overall percentage yield 70%.

(3) Using 20 g. of hydrocarbon. Yield 11.4 g. (47%). Further concentration of the liquors gave a gum which did not crystallise.

(b) Attempted preparation from tetraphenylcyclopentadienone.

Preparation of tetraphenylcyclopentadienone, (60).

20 g. of benzil and 20 g. of dibenzyl ketone were dissolved in 400 ccs. of boiling ethanol. A solution of 1 g. of potassium hydroxide in 5 ccs. of ethanol was run into the boiling solution, and after a few minutes boiling, very dark red, almost black, lustrous crystals separated from a deep red solution. The product was collected and washed with ethanol. Yield 31 g. (85%), m.p. 216°-218°C. The product required no further purification.

Reduction of tetraphenylcyclopentadienone with lithium aluminium hydride, (61).

1 g. of tetraphenylcyclopentadienone and 50 ccs. of sodium dried n-butyl ether were placed in a flask fitted with a stirrer, a dropping funnel and a water condenser guarded by a calcium chloride tube. The flask was cooled in an ice bath. 1 g. of lithium aluminium hydride in 50 ccs. of dry ether was added fairly rapidly and the mixture stirred for two to three hours. The purple colour was discharged and the solution assumed a yellow colour. At the end of the stirring, hydrolysis was effected by addition of dilute hydrochloric acid. The ether layer was separated and dried over magnesium sulphate.

Action of phosphorus tribromide on Reduction Product.

The ethereal solution was treated with phosphorus tribromide. The resultant mixture was washed with water and extracted with benzene. Evaporation of the solvents left an intractable gum.

Preparation of pyridinium 2:3:4:5-tetraphenylcyclopentadienylide.

1 g. of bromotetraphenylcyclopentadiene was allowed to stand overnight with 12 ccs. of pyridine. The solution soon became deep red in colour and a yellow precipitate of N-(2:3:4:5-tetraphenylcyclopentadienyl)-pyridinium bromide was deposited, which was washed with petroleum ether to remove any excess pyridine. Yield 1.09 g. (93%). After one recrystallisation from alcohol, m.p. 213.5°-215.5°C. (Analyses - 11, 12, 18.)

Treatment of the chloroform suspension of this salt with water gave a blue coloration in the organic layer. This effect was accelerated by addition of a little sodium hydroxide. The blue coloured material was obtained solid by alkaline treatment of an aqueous-acetone suspension of the salt.

0.4 g. of N-(2:3:4:5-tetraphenylcyclopentadienyl)-pyridinium bromide was suspended in water with a little alcohol added. A few drops of dilute sodium hydroxide solution were added and the mixture allowed to stand for several hours at room temperature. A very dark blue

crystalline material was deposited. Yield 0.28 g. (82.5%), m.p. 208°-210°C.

The ylide could not be recrystallised from any of the usual solvents but analysis samples were prepared from recrystallised samples of the intermediate bromide and washed thoroughly with sodium hydroxide solution, and then water, each containing a little alcohol. (Analyses:- 15. 19.)

The preparation of pyridinium tetraphenylcyclopentadienylide was repeated to provide material for other experiments. The yields of intermediate bromide were 87%, 95%, 94.5%, and of the ylide 82.5%, 95% and 88%.

Both the bromide and the ylide were completely insoluble in water, and the former did not react except in the presence of an organic solvent.

Reaction of other organic bases with 1-bromo-2:3:4:5 tetraphenylcyclopentadiene.

α-Picoline.

0.5 g. of the bromo compound was allowed to stand with approximately 6 ccs. of α-picoline at room temperature. The colour of the solution deepened gradually, and after standing overnight had assumed a reddish tint. After two or three days a light brown crystalline deposit was filtered off and washed with petroleum ether.

Yield of N-(2:3:4:5-tetraphenylcyclopentadienyl)-α-picolinium bromide 0.036 g. (6%) m.p. 192°-194°C.

A second preparation using 0.4 g. of the bromo compound and 2 ccs. of α-picoline gave 0.056 g. of product (11.9%).

Treatment of an aqueous alcoholic suspension of the bromide with sodium hydroxide solution gave a precipitate of reddish purple material, which dissolved in benzene to give a blue solution, in a manner exactly comparable with the unsubstituted ylide.

β-Picoline.

0.5 g. of the bromo compound was allowed to stand with approximately 6 ccs. of β-picoline. The solution rapidly became a deep red-purple colour. After two to three days a buff coloured solid was filtered off, and washed with petroleum ether.

Yield of N-(2:3:4:5-tetraphenylcyclopentadienyl)-β-picolinium bromide 0.46 g. (76.1%), m.p. (after two recrystallisations from ethanol) 206°-208°C. The yield from an experiment using 0.4 g. of bromo compound and 2 ccs. of β-picoline was 0.27 g. (56.2%). (Analysis, 37.)

A red-purple ylide, colouring a benzene solution deep blue, was formed in exactly the same way as before.

γ-Picoline.

0.5 g. of the bromo compound was allowed to stand for several days, at room temperature, with approximately 12 ccs. of γ-picoline. After a few minutes the liquors were coloured a deep reddish purple. The N-(2:3:4:5-tetraphenylcyclopentadienyl)-γ-picolinium bromide was

filtered off and washed with petroleum ether. Yield 0.405 g. (67%), m.p. (after two recrystallisations from ethanol) 218°-220°C. (Analysis 16, 20.)

Repeat experiments using less γ-picoline in proportion to the amount of bromo compound gave yields of 69% and 93%.

0.105 g. of the bromide was converted into the corresponding ylide by suspending in an aqueous alcoholic mixture and treating with sodium hydroxide solution. After standing overnight the blue-purple crystalline product which imparted a deep blue coloration to its benzene solution, was filtered off and washed well with sodium hydroxide solution containing a little alcohol. Yield 0.074 g. (89.3%), m.p. 208°-210°C. (Analyses 17, (sample prepared by reprecipitation with sodium hydroxide solution of a solution in glacial acetic acid), 21, (sample prepared from recrystallised hydrobromide).)

2:6-Lutidine.

0.5 g. of the bromo compound was allowed to stand with approximately 6 ccs. of 2:6-lutidine for two to three days. The colour of the liquors slowly became red. A grey-green powder was filtered off and washed with petroleum ether. Yield 0.17 g.

This product was much more soluble in alcohol than the previous ones, and was recrystallised by precipitation from alcoholic solution with ether, m.p. 208°-210°C.

The product before crystallisation gave the familiar

red-blue colour on treatment with alkali. However, after recrystallisation it gave no such reaction.

Analyses (40, 44) have a much better agreement with a formula representing the hydrobromide of the base, than with one for the hydrobromide of the ylide. Thus the product was in all probability 2:6-lutidine hydrobromide, contamimated with a little of the required product which was removed by recrystallisation. The yield recorded represents about 80% recovery of bromine, as lutidine hydrobromide.

This conclusion was confirmed by preparation of a picrate from the salt. After recrystallisation from ethanol this melted at 158°-160°C. Analysis (41), agreed reasonably with that required for lutidine picrate.

isoQuinoline.

0.5 g. of the bromo compound was allowed to stand for about ten days with approximately 0.3 g. of isoquinoline in a few ccs. of benzene. The liquors very slowly turned red. A brown solid product was filtered off and washed with petroleum ether. Yield 0.09 g., m.p. 205°-211°C.

As with the product from 2:6-lutidine, this was probably mainly the hydrobromide from isoquinoline. A picrate was prepared from it whose analysis figures, (47) fitted reasonably for isoquinoline picrate. The sample was recrystallised from boiling water and had m.p. 220.5°-223.5°C. Mixed m.p. with isoquinoline picrate

(m.p. 226°-228°C) was 218°-220°C.

Nevertheless, alkaline treatment of the brown salt gave a blue precipitate, which faded to grey after standing over the weekend. An analysis sample was prepared by dilution of a hot alcoholic solution with water. The analysis, (48), had a nitrogen value only half that expected for the ylide.

Quinoline.

0.5 g. of the bromo compound was allowed to stand with 4 ccs. of quinoline. After a few days the bromo compound had dissolved, but no salt was precipitated even after allowing to stand for three months, and diluting with petroleum ether. However, on addition of sodium hydroxide solution, a blue precipitate was formed. No further work was done on this as the presence of the quinoline prevented the proper collection of this precipitate.

5:7-dimethyl-2:3-benzo-1:4-diazepine.

0.5 g. of the bromo compound and 0.2 g. of the diazepine were allowed to stand with a few ccs. of benzene for several days. No reaction was observed, and no materials giving rise to coloured products on alkaline treatment were obtained, even on refluxing the reactants with nitromethane.

4:5-Diphenyl glyoxaline.

0.5 g. of the bromo compound and 0.25 g. of diphenyl glyoxaline were allowed to stand with a few ccs. of a mixture of benzene and nitromethane. The mixture was

treated as in the previous experiment but with a similar lack of success.

Products from the mother-liquors in reactions of bromotetraphenylcyclopentadiene with pyridines.

The filtrates obtained on collection of the hydrobromides from the reaction of bromotetraphenylcyclopentadiene with pyridine and α-, β-, γ-picolines were set aside. On prolonged standing, or on dilution with water, a dark reddish brown solid was deposited. This solid in no case gave a colour reaction with sodium hydroxide.

The product in each case was shown to be the same, and to be almost entirely tetraphenylcyclopentadienone. This was established by melting points and mixed melting points of the individual products, and of their Diels Alder adducts with maleic anhydride.

Preparation of Diels Alder adducts.

The reaction of tetraphenylcyclopentadienone with maleic anhydride has been described by Allen and Sheps, (79).

1 g. of tetraphenylcyclopentadienone and 1 g. of maleic anhydride were heated together cautiously in a conical flask, using an oil bath at 150°-160°C. The heating was continued until the red colour of the tetraphenylcyclopentadienone had disappeared. The residual light brown solid was crystallised from benzene. A white crystalline product was obtained from pink benzene liquors. Yield 0.6 g., m.p. 221°C.

A small quantity of the solid material from the pyridine and α- and β-picoline liquors was treated with an approximately equal amount of maleic anhydride as above. The benzene liquors were coloured pale brown.

Melting points (in °C.):-

Tetraphenylcyclopentadienone	216°-218°	Mixed m.p. with tetraphenylcyclopentadienone
Product from pyridine liquors	210°-215°	210°-215°
Product from α-picoline liquors	210°-215°	212°-215°
Product from β-picoline liquors	214°-216°	210°-215°

Maleic anhydride adducts with:-		Mixed m.p. with adduct from tetraphenylcyclopentadienone.
Tetracyclone	221°	
Product from pyridine liquors	216°	222°
Product from α-picoline liquors	220°-222°	218°-220°
Product from β-picoline liquors	indistinct	---

The adduct formed from the β-picoline product was contaminated with maleic anhydride which, melting early, masked the melting points.

Attempted preparation of ylides from 2:5-diphenylcyclopentadiene.

Reaction of the hydrocarbon with N-bromosuccinimide.

1 g. of 2:5-diphenylcyclopentadiene and 0.82 g. of N-bromosuccinimide were refluxed together in 20 ccs. of carbon tetrachloride for about three hours, and then allowed to stand overnight. The succinimide was filtered

off and the filtrate evaporated under reduced pressure. A dark tarry product, which did not crystallise well on trituration, was obtained. Yield 0.73 g.

Although it was not certain that the required product had been obtained, it was allowed to stand overnight with 2 ccs. of pyridine. A red-brown solution was formed, but no solid separated. No coloured materials were obtained on treatment of the mixture with sodium hydroxide solution.

Addition of bromine to 2:5-diphenylcyclopentadiene.

1 g. of the hydrocarbon was dissolved in about 20 ccs. of chloroform, and a solution of 0.25 ccs. of bromine in a little chloroform was run into the stirred, cooled solution over about half an hour. Some of the chloroform was sucked off, and 0,75 ccs. of pyridine were added. The deep green colour of the solution was discharged to give a brown solution. After allowing to stand for a few hours the chloroform was removed at the water pump. The sticky residue gave no coloured product with sodium hydroxide solution, nor did it give a picrate on treatment with an alcoholic solution of picric acid.

Reaction of bromotetraphenylcyclopentadiene with diphenyl sulphide.

2.7 g. of bromotetraphenylcyclopentadiene, 1.1 g. (1 cc.) of diphenyl sulphide and about 15 ccs. of nitromethane were mixed and allowed to stand overnight at room temperature. No reaction appeared to have taken place, and the solid residue on filtration had the same melting point as bromotetraphenylcyclopentadiene. Treatment with aqueous alcoholic sodium hydroxide solution produced no colour change.

The filtrate and residue were recombined, a few drops of diphenyl sulphide added, and the mixture refluxed for nineteen hours, spread over three days. The light brown solid residue obtained on filtration was unreacted bromotetraphenylcyclopentadiene. The filtrate was evaporated down but the product again was unreacted starting material.

Reaction of bromotetraphenylcyclopentadiene with dimethyl sulphide.

Samples of 0.5 g. of bromotetraphenylcyclopentadiene and approximately 20 ccs. of (a) nitromethane, and (b) benzene were allowed to stand overnight at room temperature, with 0.1 cc. of dimethyl sulphide. No change had apparently taken place in either case, so a little more dimethyl sulphide was added and the mixtures allowed to stand for two months.

(a) A small solid deposit was filtered off. This was a dark red crystalline solid, resembling tetraphenylcyclopentadienone, m.p. 215°-221°C.

The solvents were removed from the filtrate, and a dark, sticky residue was obtained. Rubbing on a porous plate gave a brown solid of indeterminate melting point about 100°C.

This residue was extracted with hot acetone, and the acetone evaporated to yield 0.44 g. of a dark solid, again with melting point indistinct but about 100°C. This material showed no reaction with sodium hydroxide solution containing alcohol or acetone.

Recrystallisation of a sample from hot alcohol gave a dark red solid, m.p. 208°-211°C, (red melt) which did not depress the melting point of tetraphenylcyclopentadienone.

(b) The benzene was evaporated, leaving 0.43 g. of a reddish black crystalline solid, m.p. approximately 150°C.

This material was also identified after recrystallisation from ethanol, by means of melting point and mixed melting point determinations, as tetraphenylcyclopentadienone.

Reaction of dibromocyclopentene with dimethyl sulphide.

9.7 ccs. of dibromocyclopentene solution 'B' were mixed with 2.5 ccs. (2.1 moles) of dimethyl sulphide, and the mixture allowed to stand at room temperature. After a few hours a buff, sticky precipitate began to form and after one or two days the supernatant liquors were decanted, and the

traces of chloroform remaining removed at the water pump at room temperature.

Yield of involatile material 5.43 g. The residue, which did not crystallise even on trituration with ether, acetone or alcohol, was taken up in water and 40% aqueous sodium hydroxide solution added. A red-brown oily precipitate was obtained, which was extracted into chloroform. The chloroform extract was dried for a few minutes with drierite, and the solvent removed at room temperature and reduced pressure. The sticky red residue, yield 1.3 g. (63%) was obtained solid by rubbing on a porous plate, and could then be recrystallised from a methanol/chloroform mixture to yield a red brown solid, which did not melt at 300°C, but decomposed slowly on heating. (Analysis 7Ø).

The colour of the solution varied slightly with the solvent, being yellow in benzene, in which it is very sparingly soluble, orange in chloroform and orange-red in methanol and acetone.

The colour of a chloroform solution was almost completely discharged by acid, and restored by alkali.

Bis-(dimethylsulphono)-cyclopentene dipicrate.

In a similar experiment, 1.75 g. of the involatile intermediate were dissolved in alcohol and treated with picric acid solution. A yellow picrate was precipitated and collected by filtration. Yield 0.62 g. (20%).

A sample of this picrate was treated with 40% sodium hydroxide solution, and allowed to stand overnight, but no coloured materials, extractable into chloroform or methylene dichloride, were formed even on heating almost to boiling.

After three recrystallisations from boiling water, the picrate melted at 162°-164°C (with decomposition). The analysis (68), was correct for bis-(dimethylsulphono)-cyclopentene dipicrate.

Derivatives of the sulphonium ylide.

Picrate.

A solution of the red-brown ylide in methanol was treated with picric acid solution. A dirty yellow precipitate was formed, but on filtration this formed an intractable gum as soon as the solvent was removed.

Chloranil adduct.

On adding a little of the ylide to a solution of chloranil in benzene, a deep blue colour, which faded slowly, was imparted to the solution.

Diazo product.

0.1 cc. of aniline was reacted with the calculated amount of sodium nitrite in dilute hydrochloric acid, the temperature of the mixture being kept between 0° and 5°C. This diazonium solution was added to 0.1 g. of the ylide in aqueous methanolic suspension, and the mixture allowed to stand for one hour. A deep red colour was produced, which was not apparently deepened by the addition of sodium

hydroxide solution. A red solid was precipitated and collected by filtration. Yield (crude) 0.18 g. (100%).

Recrystallisation was effected from a benzene/carbon tetrachloride mixture by precipitation with petroleum ether. No distinct melting point was observed, but the material decomposed over a range 130°-150°C. Analysis (72), agreed with the expected values on nitrogen only.

The diazo derivative formed neither a picrate nor a chloranil adduct under the usual conditions.

Preparation of 2:6-dimethyl-γ-pyrone, (80).

(1) 2 g. of dehydracetic acid were boiled with 25 ccs. of concentrated hydrochloric acid until the effervescence ceased, which took half to three quarters of an hour. The solution was transferred to an evaporating dish and evaporated almost to dryness. The residue was taken up in water, neutralised with sodium hydroxide solution and again evaporated almost to dryness. A watch glass was placed over the dish in the latter stages to prevent loss of the product by sublimation. The residue was transferred to a vacuum sublimation apparatus and sublimed at temperatures raised gradually to 160°C, under 1 mm. pressure. A white crystalline product came out on the cool upper surfaces of the tube. Yield 0.55 g. (37.1%), m.p. 128°-130°C.

The residue from the sublimation tube was taken up in water, and extracted with chloroform. The organic layer was coloured slightly yellow but yielded a negligible amount of solid material on evaporation.

(2) A similar experiment was carried out, but instead of evaporating down the acid solution it was neutralised with sodium hydroxide solution, and extracted with chloroform. The extract was dried overnight over anhydrous sodium sulphate and the chloroform removed to give a white, crystalline solid. Yield 1.05 g. (70.9%), m.p. 129°-130°C.

(3) A similar experiment was carried out using 80 g. of dehydracetic acid and 1000 ccs. of concentrated hydrochloric acid. The solution was boiled in a beaker for several hours to reduce the amount of hydrochloric acid to be neutralised. After neutralisation with sodium hydroxide, extraction with chloroform, drying of the extract and removal of the solvent, a pale brown crystalline material was obtained. Yield 47.4 g. (80.3%), m.p. 130°-134°C.

One recrystallisation from a benzene/petroleum ether mixture yielded 38 g. (64%) of a white crystalline material m.p. 132°-134°C.

(4) Experiment (3) was repeated using 100 g. of dehydracetic acid and 1250 ccs. of hydrochloric acid. No solid material was obtained, even on addition of further alkali to the aqueous layer and a second extraction with chloroform.

(5) Experiment (4) was repeated exactly. 61.5 g. (83.3%) of pale brown crystalline product, m.p. 130°-134°C were obtained. One recrystallisation gave 55.5 g. of white material. On standing the liquors deposited a second crop of 5.5 g. of white material. Total 61 g. (82.5%) m.p. 132°-134°C.

Attempts at the preparation of tetraphenylcyclopentadienyl magnesium bromide and iodide.

In all the work done on this topic the same apparatus was used, namely, a three-necked, round-bottomed flask carrying a condenser and a dropping funnel (both guarded

by Calcium chloride tubes), and a stirrer with a mercury seal. The apparatus was dried in an oven at about 110°-120°C before use.

The magnesium used (Grignard grade) was degreased with ether, dried first in a vacuum desiccator, and then in the reaction flask by playing a luminous Bunsen flame on the outside of the flask for several minutes before each run was set up.

The ether and benzene used were rigorously dried with sodium. Methyl iodide and ethyl bromide were dried over sodium sulphate, and distilled in dry apparatus with the receiving flask guarded by a calcium chloride tube. All solid materials used were dried thoroughly and then kept over phosphorus pentoxide in a vacuum desiccator.

Direct Method.

The direct method involving the reaction of magnesium with bromotetraphenylcyclopentadiene was tried several times without success. 0.15 g. of magnesium were used, a little ether added and a solution of 2.5 g. of the bromo compound in benzene gradually added. No heat of reaction was observed, and the reaction was not initiated by crushing the magnesium with a glass rod, addition of crystals of iodine, addition of a little methyl iodide, or by warming to the boiling point of ether.

Exchange reaction of tetraphenylcyclopentadiene with methyl and ethyl magnesium bromide.

Initially difficult was encountered in the preparation of the simple Grignard reagents, and there was always a certain reluctance for these reactions to start. A distinct improvement was made by using a smaller volume of ether both to cover the magnesium and to make up the alkyl halide solution. On addition of the tetraphenylcyclopentadiene no heat of reaction was observed in any of the several runs, and there was no apparent evolution of gas (methane or ethane) even on stirring and refluxing on an isomantle for 1-2 hours. The quantities used were 0.15 g. of magnesium, 0.4 - 0.6 ccs. of methyl iodide (or ethyl bromide - a slight excess in each case) and 2 g. of tetraphenylcyclopentadiene.

Reaction with 2:6-dimethyl-γ-pyrone and tetraphenylcyclopentadienone.

Despite the lack of evidence for the formation of the required organo-magnesium compound, the reaction of the "Grignard solution", described above, with 2:6-dimethyl-γ-pyrone and tetraphenylcyclopentadienone was tested.

(i) To the solution obtained in one of the attempted exchange reactions was added, with mechanical stirring, a benzene solution of 0.78 g. of the γ-pyrone. After stirring for about half an hour the mixture was decanted into a cold perchloric acid solution. The layers were separated, and each was tested with acid and alkali, but

no colour change was observed. The starting materials were recovered in reasonable yields - the hydrocarbon from the benzene, and the pyrone by chloroform extraction of the aqueous layer, after it had been made alkaline.

(ii) Grignard solutions as prepared above were treated with 1.6 g. of tetraphenylcyclopentadienone, in benzene solution. In no case was the colour of the tetraphenylcyclopentadienone discharged even after the mixture had been refluxed for periods of from a few hours to two days. The starting materials were recovered almost completely and separated roughly by crystallisation from alcohol. The two fractions obtained in this way were chromatographed on an alumina column (4 cm. x 10 cm.). The tetraphenylcyclopentadienone and tetraphenylcyclopentadiene were rather difficult to separate completely, despite the difference in colour, but no appreciable amount of any other material was observed in the eluates, even when the column was illuminated in U.V. light during the separation.

Attempted reaction between cyclopentadienyl magnesium bromide and 2:6-dimethyl-γ-pyrone.

Ethyl magnesium bromide was prepared from 1 g. of magnesium and 3.6 ccs. of ethyl bromide (slight excess). 3.4 ccs. (2.75 g.) of cyclopentadiene (freshly distilled under anhydrous conditions), in ether solution, were run in gradually over about half an hour, with rapid stirring.

There was little heat of reaction, but there was some evidence of gas evolution. After two hours stirring a benzene solution of 5 g. of 2:6 dimethyl-γ-pyrone was run in rapidly. A red brown oil was produced, and after a few minutes the reaction mixture was divided into two portions. One was hydrolysed by adding it to cold ammonium chloride solution, the other by adding it to cold dilute perchloric acid solution.

The two mixtures were treated in the same way. The oil dissolved in the upper organic layer, the layers were separated and the organic layers dried and distilled. The residue in each case was non-crystalline, and smelt strongly of cyclopentadiene (possibly the dicyclopentadiene had been reformed).

The aqueous layers were extracted with chloroform, and the extracts yielded 2.9 g. of 2:6-dimethyl-γ-pyrone. The remaining aqueous layers contained a small amount of dissolved green material, which could not be extracted into organic solvents under either acid or alkaline conditions.

Preparation of sodio tetraphenylcyclopentadiene.

A dry one litre three-necked flask was embedded in sawdust in a basin and about 100 ccs. of liquid ammonia run in. Two of the necks of the flask were stoppered, the third carried a soda lime tube pointing into the fume cupboard in which the operation was carried out. A few crystals of ferric nitrate were added, followed by 0.25 g.

of clean sodium, cut into small pieces. 2 g. of tetraphenylcyclopentadiene were added, with occasional swirling, to the solution of sodamide in ammonia, which had assumed a blue colour. After two hours, about 70 ccs. of dry benzene were run in and the ammonia allowed to evaporate.

This preparation was repeated and one batch was treated with tetraphenylcyclopentadienone, the other with 2:6 dimethyl-γ-pyrone.

Reaction with Tetraphenylcyclopentadienone.

The flask containing the sodio compound was fitted with a mercury sealed stirrer and a dropping funnel. 1.9 g. of tetraphenylcyclopentadienone in dry benzene were run in, with stirring. The stirring was continued for about two hours by which time the red colour of the ketone had apparently disappeared leaving a dark brown solution. Hydrolysis was effected by addition of dilute acetic acid to the stirred solution. After fifteen minutes the benzene layer was separated, the aqueous layer extracted with benzene and the combined benzene layers dried over calcium chloride. The benzene was removed on the water bath and a brown residue, weight 3.56 g., was obtained.

1.16 g. of this material was extracted with hot alcohol, and the extract filtered. 0.3 g. of a solid with a green tinge was retained on the filter. This proved to be almost entirely tetraphenylcyclopentadienone, but by

chromatography on alumina (2 x 15 cm.) a small amount of a red-orange gum was separated. This was obtained solid by trituration with acetone, and melted at 172°-177°C. It depressed the melting point of tetraphenylcyclopentadiene (m.p. 178°C). Analysis (56), did not correspond to the expected formula.

The alcoholic filtrate was evaporated, and 0.6 g. of a brown residue was obtained. The melting point was in the range of 100°-120°C. Recrystallisation from methanol was difficult, as the material melted under the liquid and formed a gum. Purification was effected by chromatography on alumina (1.5 x 17 cm.), the main eluate being taken. A crystalline sample was prepared by taking up the residue, after removal of the solvent, in alcohol, filtering and precipitating with a little cold water. M.p. 110°-113.5°C. Again analysis (57), gave no helpful results.

Attempted dehydration.

0.2 g, of the brown residue, after evaporation of the alcoholic filtrate, was refluxed overnight with 0.02 g. of iodine in a few ccs. of benzene (cf. 66). The solvent and iodine were removed at the water pump on the water bath. The residue was redissolved in benzene, the solution applied to an alumina column (15 x 2 cm.), and developed and eluted with ether. Only starting material was detected in the eluates.

Reaction with 2:6-dimethyl-γ-pyrone.

The flask containing the sodio compound was fitted with a mercury sealed stirrer and a dropping funnel. 0.7 g. of 2:6-dimethyl-γ-pyrone in benzene solution was run in with stirring, which was continued for ten minutes. There was little change in the colour of the solution. The mixture was hydrolysed by adding dilute acetic acid, the layers separated, the aqueous layer washed with benzene, andthe benzene layers combined and dried over calcium chloride. The benzene was removed under reduced pressure and a brown glass remained. Trituration with ether and alcohol did not induce crystallisation but on shaking with a little acetone and then pumping off the acetone a voluminous plastic like material was formed. This could be crumbled to a brown powder. Yield 2.68 g. After two recrystallisations from methanol the m.p. was 128.5°-131.5°C. Mixed m.p. with 2:6-dimethyl-γ-pyrone (m.p. 132°-134°C) was approximately 110°C. Analysis (59) was inconclusive.

Attempted dehydration.

0.2 g. of the brown powder was refluxed overnight with 0.02 g. iodine in a few ccs. of benzene. The benzene and iodine were removed on the water bath using a water pump, the residue taken up in a benzene/acetone mixture and applied to an alumina column (1.2 x 15 cm.). The

first eluate (with ether as eluant) was the only one to give any crystalline material. This was a yellow crystalline solid, weight 0.037 g., m.p. 81°-85°C. Analysis (60), again was inconclusive.

Derivatives of pyridinium cyclopentadienylide.

Picrate.

Addition of ethanolic picric acid solution to a hot solution of the ylide in benzene or ethanol resulted in the formation of yellow precipitates which darkened rapidly.

A picrate was prepared from cold filtered solutions of the ylide in benzene, and picric acid in ethanol. A yellow-brown precipitate was formed and collected by filtration. The material was very sensitive to heat, and attempts at recrystallisation led to decomposition of the picrate. An analysis sample was therefore prepared by washing the precipitate well with benzene and ether, m.p. decomposes ca. 95°C. (Analysis, 64.)

Methiodide.

0.1 g. of pyridinium cyclopentadienylide was shaken with a little methyl iodide in ether, the flask having previously been flushed out with nitrogen. No change was observed after shaking for a day.

Trinitrobenzene adduct.

Pyridinium cyclopentadienylide, in alcoholic solution, was treated with trinitrobenzene. After standing for 1-2 days only starting materials were detected in the product.

Adducts with chloranil and benzoquinone.

Filtered benzene solutions of the ylide were treated respectively with filtered benzene solutions of chloranil and benzoquinone.

In each case a deep coloration, purple with benzoquinone and greenish blue with chloranil, was produced immediately. These colours faded after about one minute.

A dark coloured precipitate was collected from the benzoquinone reaction, washed with benzene and water and a sample sent for analysis (52). The figures showed this to be slightly impure benzoquinone.

Analysis of a similar product from the chloranil experiment gave a corresponding result. Any complex which had formed, therefore appeared to have decomposed rapidly.

Reactions of Pyridinium cyclopentadienylide.

Bromination.

0.345 g. of the ylide was taken, dissolved in chloroform, and the solution run into a three-necked flask fitted with a dropping funnel and nitrogen inlet and outlet tubes. The apparatus was previously flushed out with nitrogen which had been passed through a mercury bubble bottle and a calcium chloride drying tower. The outlet tube led into a trap cooled in salt and ice, and then by means of rubber tubing and a small inverted funnel (to prevent sucking back) into water contained in a small beaker.

A gentle stream of nitrogen was passed through the reaction flask, and a solution of one molar equivalent of bromine in chloroform was run in slowly. The rich red

colour of the ylide solution was discharged and a dark solid deposit obtained. At the end of the addition no bromine had collected in the cold trap, and apparently no hydrogen bromide had been evolved as the solution in the beaker was neutral to litmus.

The solid deposit was filtered off and washed with chloroform. It was a brown powder, insoluble in chloroform or methylene dichloride and very slightly soluble in acetone. It was soluble in alcohol and water, and could be precipitated from methanol by addition of ether. As heating even to the boiling point of methanol caused decomposition, an analysis sample was prepared by adding ether to a filtered methanolic solution.

Yield 0.3 g. No melting point could be determined, as the material decomposed on heating. Analysis (49) did not correspond to any simple bromination product, although the percentage of bromine was that for a compound in which one atom of bromine had been introduced.

Reaction with Maleic Anhydride.

An apparatus similar to that used for the bromination experiment was set up. 0.31 g. of pyridinium cyclopentadienylide in about 20 ccs. of benzene was placed in the flask, dry nitrogen bubbled through and 0.25 g. of maleic anhydride in benzene was added. The deep red colour of the ylide was gradually discharged, and after about 20 minutes the inlet and outlet tubes were closed,

and the mixture allowed to stand overnight in an atmosphere of nitrogen.

A brown precipitate settled out from the pale brown liquors, and this was collected and washed well with benzene. The washings were pink indicating the presence of some unreacted ylide. Yield 0.24 g. On heating, the product decomposed to give a black residue, and did not melt below 270°C.

The brown material was practically insoluble in organic solvents, and an analysis sample was prepared by thorough washing with benzene and ether.

It was more soluble in dilute sodium hydroxide solution, to give a red-brown solution. Extraction with benzene or chloroform gave to some extent the familiar red colour of the ylide in the organic layer. This suggested that perhaps a salt had been formed between the maleic anhydride and the ylide. The analysis (51) fitted for no simple adduct.

Coupling with benzene diazonium chloride.

0.1 cc. of aniline was reacted with the calculated amount of sodium nitrite in dilute hydrochloric acid, the temperature being kept between 0° and 5°C. This diazonium solution was added to 0.1 g. of pyridinium cyclopentadienylide in an aqueous methanol suspension. The red colour of the ylide solution deepened, and when made alkaline with dilute sodium hydroxide solution, a

dark coloured precipitate formed. Yield 0.164 g. (90%). The product decomposed on heating in a melting point apparatus.

The colours of the solutions of the diazo compound in organic solvents were deeper than those of the solutions of the ylide itself, so that benzene and chloroform were coloured deep red-purple and the alcoholic solution was bright red.

Recrystallisation was attempted from a range of organic solvents but no satisfactory method was found. An analysis sample was prepared by evaporation of the solvent from a filtered benzene solution.

The figures obtained (53) corresponded approximately to a compound with one diazo group.

Reaction with acetyl bromide (cf 19).

0.335 g. of pyridinium cyclopentadienylide was placed in a three-necked flask fitted with a dropping funnel, mercury-sealed stirrer and a condenser with a calcium chloride tube. 50 ccs. of sodium-dried benzene, and a few drops of pyridine were added. The stirrer was started and a solution of 0.2 cc. of acetyl bromide in sodium-dried benzene was run in over about half an hour. The stirring was continued for one and a half hours, and the dark brown deposit which had formed was filtered off, and washed with a little benzene. The precipitate which had appeared granular, became a gum on removal of the last traces of solvent.

This could not be crystallised by trituration with methanol or acetone. Its methanolic solution was chromatographed on filter cel, but the eluates gave no solid product. As the product appeared to be hygroscopic, it was allowed to stand over concentrated sulphuric acid overnight in a vacuum desiccator. A trace only of crystalline material was obtained in this way.

An analysis sample (58) was prepared from this material by washing with methanol, and drying in vacuo over concentrated sulphuric acid.

The product did not give an oxime or a dintrophenyl-hydrazone, even after refluxing with the reagent for several hours.

Condensation of o-nitrobenzaldehyde with γ-picolinium and pyridinium cyclopentadienylides. (cf 67).

0.25 g. of γ-picolinium cyclopentadienylide and an equal amount of o-nitrobenzaldehyde were dissolved in alcohol, a few drops of piperidine were added, and the mixture was allowed to stand. After a few hours a dark coloured product settled out on the walls of the flask. After standing overnight the black deposit was filtered off. Yield 0.5 g.

This material was difficult to recrystallise, but an analysis sample was obtained by dilution of a pyridine solution with water. It did not melt below 350°C.

The possible significance of the analysis (10) is discussed in the Theoretical Section.

A similar experiment was set up using pyridinium cyclopentadienylide, but only unchanged starting materials were obtained. Attempts to repeat the first reaction were unsuccessful.

Condensation of cyclohexanone with pyridinium and γ-picolinium cyclopentadienylides.

0.1-0.2 g. of clean sodium was dissolved in 30 ccs. of methanol, and to the cooled solution was added 0.5 cc. of purified cyclohexanone (see below) and a suspension of 0.53 g. of pyridinium cyclopentadienylide in 20 ccs. of methanol. The mixture was allowed to stand with occasional shaking for about twenty-four hours. The colour of the solution had not changed, and on diluting with water and extracting with chloroform most of the ylide was recovered unchanged.

A similar reaction was set up using 0.6 cc. of cyclohexanone and 0.64 g. of γ-picolinium cyclopentadienylide. As in the last experiment there was no reaction, even after refluxing for four hours.

Purification of cyclohexanone.

40 g. of sodium bisulphite were dissolved in approximately 70 ccs. of water (to give a saturated solution). To this solution was added 70% of its volume of methylated spirits, and then just enough water to give a clear solution.

20 ccs. of technical cyclohexanone were poured in with stirring, and the mixture allowed to stand with occasional agitation for half an hour. The white crystalline precipitate was filtered off, transferred to a separating funnel, and decomposed with 80 ccs. of dilute sodium hydroxide solution. The cyclohexanone layer was separated. The aqueous layer was saturated with salt and extracted with 30-40 ccs. of ether. The combined organic layers were dried overnight over anhydrous sodium sulphate. The ether was removed and the residue distilled. The fraction, b.p. 152°-156°C, was collected. Yield 6.6 g.

Derivatives of pyridinium tetraphenylcyclopentadienylide.

Picrates.

On treatment of a hot alcoholic solution of either the ylide, or bromide, with a saturated alcoholic picric acid solution, a yellow crystalline picrate was obtained. These proved to be identical, and could be recrystallised from hot ethanol, m.p. 226°-228°C. (Analyses:- from ylide 29, from bromide 28).

The analyses indicated that the picrate had crystallised with one molecule of alcohol.

A picrate was also obtained by treatment of a hot benzene solution of the ylide with a solution of picric acid in benzene, m.p. 178°-182°C. (Analysis (sample recrystallised from benzene), 32).

The original picrate, with one molecule of alcohol, was obtained from the picrate prepared in benzene by recrystallising it from ethanol, m.p. 226°C. (Analysis 33). Recrystallisation from acetone gave a product, m.p. 175°C. Analysis (34) gives an indication that one molecule of acetone of crystallisation is present.

Trinitrobenzene adduct.

A little pyridinium tetraphenylcyclopentadienylide was dissolved in benzene and a solution of an equal amount of trinitrobenzene in benzene solution was added. No colour change was observed on standing, or on warming in a water bath.

After standing overnight, some colourless, tablet shaped crystals appeared, m.p. 115°-117°C, which proved to be trinitrobenzene, (mixed m.p. 117°-119°C).

Methiodide.

0.1 g. of pyridinium tetraphenylcyclopentadienylide was shaken with a little methyl iodide in ether. Although shaking was continued for 16-18 hours, no change was observed.

Diels Alder adduct.

0.4 g. of pyridinium tetraphenylcyclopentadienylide was shaken with 0.1 g. of maleic anhydride in benzene. The blue colour of the ylide gradually gave way to red and a yellow material was deposited on the walls of the flask, the change apparently being completed in half an hour. No

further change was observed after standing overnight. The precipitate was scraped out. Yield 0.25 g.

The crude material from the reaction was too sticky to determine its melting point. After two recrystallisations from alcohol, the melting point was 189°-192°C. Analyses (27, 31), do not correspond to any simple adduct.

Adducts with chloranil and benzoquinone.

Filtered benzene solutions of chloranil and benzoquinone were allowed to stand with filtered benzene solutions of pyridinium tetraphenylcyclopentadienylide. No colour change was observed in either case nor was there any indication of any solid deposit. The very intense blue colour of the ylide solution made it difficult to follow any reaction, but it was possible to say quite confidently that there was no evidence of complex formation.

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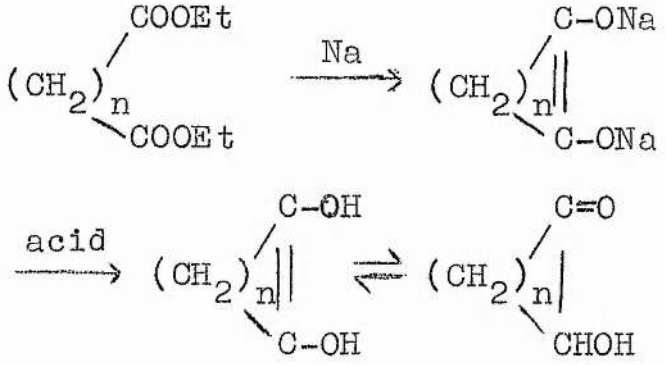
APPENDIX I.

INTRODUCTION AND THEORETICAL.

The application of pinacone reduction to the preparation of five-, six- and seven-membered rings from the appropriate diketones has been known for many years. (1, 2, 3).

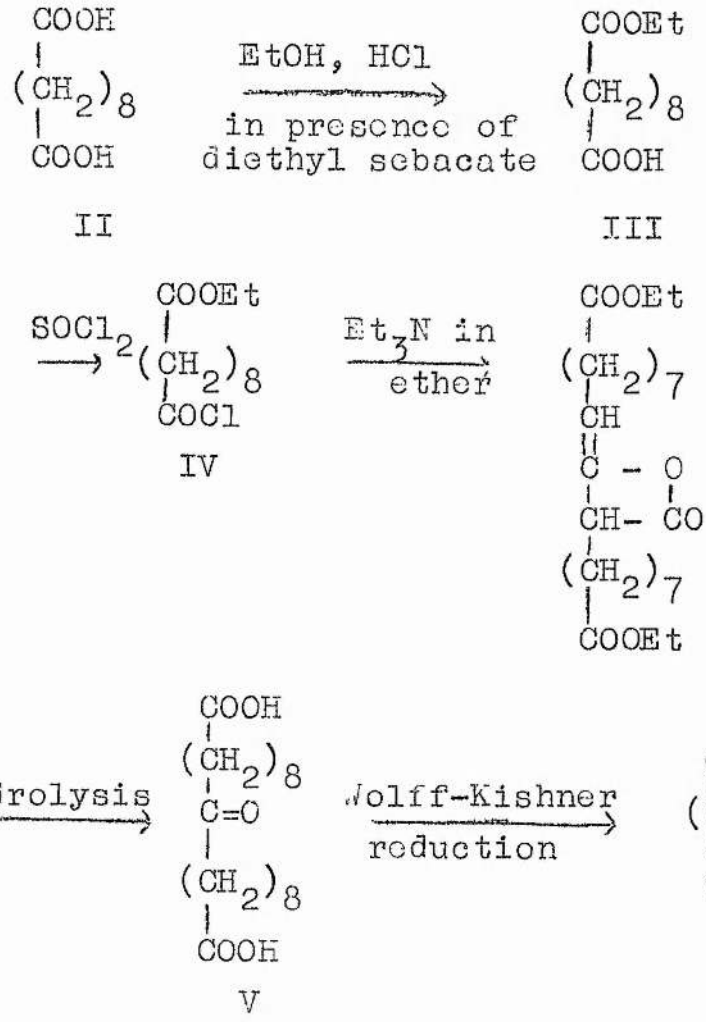
More recently the acyloin condensation has been used as a means of preparing many membered carbon rings (4, 5). This method involves the treatment of a dicarboxylic ester with sodium in boiling xylene, and a mechanism for the reaction on the surface of the metal has been suggested (4):-



Pinacone reduction resembles this reaction in that both take place on the surface of the metal, and thus it was thought possible that, if applied to a long chain diketone, ring closure might take place to give a large ring compound.

1:17-dibenzoylheptadecane was selected as a convenient diketone, which might be prepared from the acid chloride of 1:17-heptadecanedicarboxylic acid (I) by a Friedel-Crafts reaction with benzene.

The diacid was prepared from sebacic acid (II) as starting material, by the following reaction scheme:-



The first stage gave most trouble, and the yields reported in the literature (6) were never approached. The use of the Wolff-Kishner reduction in the final stage, instead of the more usual Clemmensen method, cut down reaction time considerably, but the ethylene glycol involved made separation of the product by filtration very slow.

The first attempts at the preparation of 1:17-dibenzoylheptadecane were unsuccessful. At this

time promising results were obtained from the other topic, i.e. in the investigations of the formation of cyclopentadienylides, and attention was therefore concentrated on it.

EXPERIMENTAL.

Diethyl Sebacate.

130 g. (0.65 moles.) of sebacic acid, 315 ccs. of ethanol and 25 ccs. of concentrated sulphuric acid were refluxed together for about 15 hours. The reaction mixture was diluted with approximately 500 ccs. of water, the ester layer separated, and the aqueous layer extracted with ether. The ester and ether layers were combined, washed with water, sodium carbonate, and then water again, and finally dried over sodium sulphate. The ether was removed and the residue distilled under reduced pressure, the fraction, b.p. 156°-158°C/6 mm., being collected. The fore and after runs were redistilled. Yield 100.5 g. (66.8%).

A repeat experiment was carried out using 130 g. of sebacic acid. Yield 137 g. (82.4%).

Ethyl hydrogen sebacate. (III) (6).

202 g. (1 mole) of sebacic acid, 150 g. of diethyl sebacate, 50 ccs. of redistilled n-butyl ether and 25 ccs. of concentrated hydrochloric acid (S.g. 1.19) were placed in a modified Claisen flask fitted with a reflux condenser and heated together at 160°-170°C on an oil bath. The bath temperature was then lowered to 120°-130°C and 60 ccs. (1 mole) of 95% ethyl alcohol was added, and the mixture was refluxed for two hours. The bath was again cooled, to 75°C, and the reaction mixture distilled under reduced pressure, great care being taken to avoid frothing. The

temperature was increased slowly and after water, ether and alcohol had come over, the distillation was continued at a lower pressure, using an oil pump. Diethyl sebacate distilled at 156°-158°C/6 mm. The fraction, b.p. 175°-195°C, was collected and refractionated. The ethyl hydrogen sebacate so obtained melted between 32° and 38°C.

The experiment was repeated with the following yields:-

(1) 34 g. (15.8%)

(2) 69.5 g. (30.2%)

(3) 30 g. (12.9%)

(4) 44 g. (18.9%)

(5) 35 g. (15.0%)

The fractional distillation was very difficult to carry out. To obtain a reasonable separation a long well insulated column was required, and this took a long time to heat up, and involved vigorous heating. Splashing often set in and necessitated returning products to the distillation flask.

The most successful of the various columns used was one in which the ascending vapours passed round an inner tube containing a liquid intermediate in boiling point between the two substances to be separated. The liquids used were o-dichlorobenzene (b.p. 179°C) and ethylene glycol (b.p. 197°C).

Mono-ethyl sebacyl mono-acid chloride. (IV)(7).

Ethyl hydrogen sebacate was refluxed with excess thionyl chloride for 3-4 hours at 40°C on a steam bath. The excess thionyl chloride was then distilled off and the residue used in the next stage.

The thionyl chloride used had been purified by fractionation from redistilled quinoline, and then from boiled linseed oil.

9-Keto-heptadecane-1:17-dicarboxylic acid.(V)(8).

The acid chloride from 30 g. of the half ester was added rapidly with stirring to a cold solution of 24 g. of triethylamine in 200 ccs. of dry ether under an atmosphere of nitrogen. Stirring was continued for 24 hours at room temperature, a steady stream of nitrogen being passed through all the time.

37 ccs. of concentrated hydrochloric acid were mixed with 49 ccs. of glacial acetic acid, 4-5 ccs. of this mixture were then added with stirring to the above reaction mixture, followed by 30 ccs. of water. The ether layer was separated, and the aqueous layer extracted with ether (4 x 15 ccs.)

The combined ether solutions were added to the remainder of the above mixture of concentrated hydrochloric and glacial acetic acids, the ether distilled off and the residue refluxed for six hours. This residue was evaporated on the steam bath, and 250 ccs. of concentrated

hydrochloric acid and 20 ccs. of glacial acetic acid added to the non-volatile residue, and the whole evaporated again on the steam bath. 20 ccs. of water were added and evaporated. A further 20 ccs. of water were added and the mixture heated on a steam bath for 12 hours.

It was then extracted with approximately 80 ccs. of chloroform and the acid precipitated with petroleum ether. The first fraction was collected on a filter, the filtrate evaporated down and a second crop obtained. The acid was dried in a vacuum desiccator. The m.p. of the crude keto-acid was 100°-101°C. Yield 23 g. (57.8%).

Two other runs were carried out. The first, using 50 g. of half ester, was lost; the second, using 85 g. of the half ester, gave 63.5 g. of crude keto-acid, (56.4%).

Wolff-Kishner reduction of the keto-acid. (9)

10 g. of the crude keto-acid, 3.4 ccs. of 100% hydrazine hydrate, 0.6 g. of water and 45 ccs. of diethylene glycol, were placed in a flask with a thermometer pocket and refluxed over a small Bunsen flame for 1½ hours. The condenser was then removed and excess hydrazine hydrate and water evaporated until the temperature reached approximately 200°C. The condenser was then replaced and refluxing was continued at 195°-205°C for four hours.

The cooled solution was diluted with about 45 ccs. of water and poured into approximately 6N hydrochloric acid, with stirring. The solution was filtered with difficulty.

and then washed with water and dried in a vacuum desiccator. The product was sticky, and its weight indicated more than a 100% yield, m.p. 99°-101°C. Subsequent recrystallisation from benzene and ethyl acetate gave a light buff powder, m.p. 110°-120°C. Yield 5 g. (50.9%).

There was quite a large loss of material in the recrystallisation from ethyl acetate.

A second run was carried out using 66.5 g. of crude keto-acid. Yield 35 g. (54%).
Recrystallisation from alcohol gave a product, m.p. 117°C. Analysis (14) was satisfactory for 1:17-heptadecane-dicarboxylic acid.

Attempted preparation of 1:17-dibenzoylheptadecane.

(1) 2 g. of 1:17-heptadecanedicarboxylic acid were warmed with 2.5 ccs. of thionyl chloride on a water bath at 40°-60°C, for two hours. After allowing to stand overnight, the mixture was heated for a further two hours at 40°-60°C.

The excess thionyl chloride was distilled off under reduced pressure, on the water bath. The dark brown residue was used in the next stage without further treatment.

This acid chloride and 100 ccs. of sodium-dried benzene were placed in a flask fitted with a calcium chloride tube and a dropping funnel. Fuming stannic chloride was run in dropwise to the stirred mixture, the flask being cooled in an ice bath. At the end of the addition, which took about half an hour, the cooling bath

was removed and the stirring continued for an hour, when a mixture of 1 cc. of concentrated hydrochloric acid and 4 ccs. of water was added.

The resultant mixture was warmed on the water bath, whereat most of the precipitated material dissolved in the benzene. A small amount of tarry material remained adhering to the walls of the flask. The benzene layer was separated, washed with sodium carbonate solution, then with water, dried over calcium chloride, and the solvent removed. There was no residue.

The sodium carbonate extract was acidified, and the unreacted dicarboxylic acid recovered in this way.

(2) Similar experiments were carried out using aluminium chloride as the catalyst.

4.5 g. of aluminium chloride were suspended in 25 ccs. of dry benzene in a three-necked flask fitted with a mercury sealed stirrer, a dropping tube and a condenser guarded by a calcium chloride tube. The acid chloride from 4.5 g. of the di-acid, in dry benzene, was run into the stirred suspension over half an hour and the stirring continued for a further three hours.

The reaction mixture was worked up as before. The organic layer gave a very small quantity of a non-crystalline material, which did not give a positive reaction with Brady's reagent. On acidification of the sodium carbonate extract, 3 g. of unreacted acid were recovered.

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APPENDIX II.

Analyses.

As has been mentioned earlier, throughout this work difficulty was encountered in obtaining satisfactory analysis results.

Four main factors might be responsible for this, namely:-

(i) Insufficient purity of the analysis samples.

(ii) Retention of solvent, or absorption of atmospheric moisture.

(iii) Decomposition (in particular atmospheric oxidation) of the sensitive compounds in the time lag between preparation and analysis.

(iv) A fundamental difficulty in achieving combustion of these materials.

The bulk of the analyses were carried out by Drs. Weiler and Strauss at Oxford, but some (Nos. 18, 19, 20, 21) by Mr. P.R.W. Baker, at the Wellcome Research Laboratories at Beckenham. In his work on the analysis of ylides and intermediates derived from tetraphenylcyclopentadiene, he obtained results closer to the expected values than had Weiler and Strauss. Also by dint of prolonged drying in vacuo before analysis he was able to improve further on his first figures. In Mr. Baker's opinion the last of the above factors (iv) may be discounted; he considers that numbers (ii) and (iii)

are most likely to be the source of error.

Ramirez (81), in work on the analogous triphenyl phosphonium cyclopentadienylides (48), achieved satisfactory analysis results only by arranging for immediate analysis of his products, and in such a manner as to exclude moisture in the transfer.

The sensitivity of many of the compounds in solution made it impossible to recrystallise them many times, as this would have led to a decomposed rather than a purified product. In any case the ylides, and intermediates, were normally formed in good yield, and so were unlikely to have been contaminated by large amounts of side-products or starting materials.

		Required.				Found.			
		C	H	N	Br	C	H	N	Br
2 3 5	Pyridinium cyclopentadienylide. $C_{10}H_9N$	83.9	6.3	9.8		79.5 82.5 78.0	6.0 6.8 5.98	7.7 8.2 8.3	
49	Bromination product $C_{10}H_8NBr$	54.0	3.6	6.4	36.0	45.2	3.8	4.13	36.54
51	Maleic anhydride adduct $C_{14}H_{11}O_3N$	69.8	4.55	5.8		56.58	4.82	2.95	
52	Benzoquinone (supposed adduct). $C_6H_4O_2$	66.7	3.7			67.03	4.3	0.15	
55	Chloranil (supposed adduct). $C_6Cl_4O_2$	29.26			Cl 57.72	31.21	1.06	0.59	Cl 52.82
53	Diazo compound $C_{16}H_{13}N_3$	77.72	5.26	17.0		75.53	5.11	14.5	
58	Acetyl derivative $C_{12}H_{11}ON$	77.83	5.94	7.57		42.9	4.6	6.12	
64	Picrate $C_{16}H_{12}N_4O_7$	51.6	3.23	15.05		50.46	3.68	12.5	
42 45	Intermediate:- $C_{15}H_{16}N_2Br_2$	46.87	4.16	7.29	41.66	42.85 41.44	4.84 4.77	6.63 6.85	38.07 38.9
63	$C_{10}H_{10}NBr$	53.57	4.46	6.25	35.71	43.39	4.99	6.28	37.5
43 46	Bromo derivative $C_{15}H_{16}N_2Br_4$	33.08	2.94	5.15	58.82	25.24	2.24	4.83	64.9 67.3
36 65 67	Picrate $C_{27}H_{20}N_8O_{14}$	47.62	2.94	16.45		48.1 48.41 48.21	2.81 3.05 3.08	15.2 15.6 16.1	

		Required.				Found.			
		C	H	N	Br.	C	H	N	Br.
54	Product from reaction with one molar equivalent of pyridine $C_{10}H_8NBr$	54.0	3.6	6.4	36.0	52.48	5.10	4.75	24.24
61	Picrate $C_{16}H_{11}N_4O_7Br$	42.4	2.44	12.4	17.7	49.65	3.38	12.5	10.54

		Required.				Found.			
		C	H	N	Br	C	H	N	Br
4	Reduction product:- Picrate $C_{16}H_{22}N_4O_7$	50.2	5.8	14.7		50.15	5.74	14.3	
8	γ-picolinium cyclopentadienylide					81.4	6.83	7.25	
9	$C_{11}H_{11}N$	84.1	7.0	8.9		81.03	6.76	(7.8 (7.6	
	Condensation product with o-nitro benzaldehyde $C_{18}H_{14}N_2O_2$	74.48	4.82	9.65					
10	$C_{12}H_{10}NO_3$	66.6	4.6	6.5		66.5	4.5	6.4	
	$C_{12}H_{11}NO_3$	66.35	5.07	6.45					
	Intermediate:- Picrate								
66	$C_{29}H_{24}N_8O_{14}$	49.16	3.39	15.82		49.42	3.2	15.7	
	Picrates from intermediate. Triethylamine.								
69	$C_{29}H_{40}N_8O_{14}$	48.06	5.56	15.47		48.08	5.13	13.52	
	Isoquinoline								
70	$C_{35}H_{24}N_8O_{14}$	53.84	3.1	14.35		50.83	3.01	14.4	
	$C_{15}H_{10}N_4O_7$ (isoquinoline picrate)	50.27	2.79	15.64					
62	Product from aniline					71.39	6.77	6.52	11.22
1	$C_{11}H_{11}N$	84.1	7.0	8.9		74.5	6.78	7.5	
11	Tetraphenyl-					73.43	5.28	2.72	14.9
12	cyclopentadienylides, and bromides.					71.98	5.34		
	Pyridinium.								
18	$C_{34}H_{26}NBr$	77.27	4.92	2.65	15.15	73.43	5.03		
18						74.83	5.3	(after drying)	

		Required.				Found.			
		C	H	N	Br	C	H	N	Br
15 19 19	$C_{34}H_{25}N$	91.27	5.59	3.13		88.34 90.2 90.56	5.49 5.68 5.57	3.24 (after drying)	
28 29 33 34	Picrate $C_{40}H_{28}N_4O_7 \cdot C_2H_5OH$ $C_{40}H_{28}N_4O_7 \cdot C_3H_6O$	69.8 70.29	4.71 4.63	7.76 7.63		69.6 69.87 69.7	4.84 4.71 4.52	7.84 7.65 7.35 7.3	
32	$C_{40}H_{28}N_4O_7$	71.0	4.14	8.28		65.89	4.04		
27 31	Maleic anhydride adduct $C_{38}H_{28}O_3N$	83.49	5.13	2.56		71.84 70.29	5.54 5.56	2.56	
16 20	~~α~~-picolinium $C_{35}H_{28}NBr$	77.49	5.17	2.58	14.76	74.41 77.2	5.88 5.24	2.29	14.8
17 21 21	$C_{35}H_{27}N$	91.1	5.86	3.04		81.99 89.78 90.21	5.11 5.9 5.54	2.98 (after drying)	
37	~~β~~-picolinium $C_{35}H_{28}NBr$	77.49	5.17	2.58	14.76	76.48	5.44	2.78	14.7
40	2:6 lutidinium $C_{36}H_{30}NBr$	77.7	5.4	2.51	14.39				41.13
44	$C_7H_{10}NBr$	44.67	5.32	7.44	42.55	44.63	5.11	6.0	43.7
41	$C_{42}H_{32}N_4O_7$	71.57	4.54	7.95		45.74	3.23	15.7	
	$C_{13}H_{12}N_4O_7$	46.4	3.57	16.66					
47	isoquinolinium $C_{44}H_{30}N_4O_7$	72.71	4.13	7.71		50.8	2.73	14.8	
	$C_{15}H_{10}N_4O_7$ (isoquinoline picrate)	50.27	2.79	15.64					
48	$C_{38}H_{27}N$	91.74	5.43	2.81		[illegible].54	5.6	1.25	

		Required				Found.			
		C	H	N	Br	C	H	N	Br
71	Dimethylsulphonium cyclopentadienylide $C_7H_{10}S$	66.61	7.99		S 25.41	59.09	5.84		S 6.26
72	Diazo derivative $C_{13}H_{14}N_2S$	67.79	6.13	12.16	S 13.92	65.73	5.36	12.3	S 7.05
68	Intermediate:- dipicrate $C_{21}H_{22}N_6O_{14}S_2$	39.0	3.43	13.0	9.92	39.11	2.99	13.1	9.9
56 57	$C_{58}H_{42}O$	92.28	5.56			88.9 88.67	6.13 5.14		
59	$C_{36}H_{30}O_2$	87.4	6.1			89.71	4.45		
60	'Dehydration' product $C_{36}H_{28}O$	91.8	5.89			84.59	5.62		
14	1:17-heptadecane-dicarboxylic acid. $C_{19}H_{36}O_4$	69.51	10.97			68.82	10.81		
13	Benzil $C_{14}H_{10}O_2$	80.0	4.8			79.85	4.93		